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Water Purification Associates, Cambridge, Mass

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16. ABSTRACT

The report gives results of a study to determine water consumption and environmental impacts of coal conversion processes in Western states. Part 1 gives brief descriptions and process water requirements for nine conversion processes. Detailed designs and analyses are given for the Hygas, Synthane, and Solvent Refined Coal (SRC) processes, and for Lurgi combined-cycle power generation. At three proposed sites (in North Dakota, New Mexico, and Wyoming), complete water requirements and effluents, including all mining and related off-site uses, are given for the power, Hygas, and SRC plants. The Synthane process is analyzed only at the Wyoming site. Part 2 gives analyses of influent and effluent waters, with examples for study. For the three selected plants at the North Dakota site, source water of good quality is assumed to be cheap and available. For three plants in New Mexico, source water will be available but is brackish. All the plants at the Wyoming site receive sewage from a satellite town; additional fresh water is available but is assumed to be expensive. The plants, being net consumers of water, are designed for no discharge of water. For each process at each site (10 cases) an integrated water treatment plant block flow diagram is given with approximate costs and energy requirements.

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CONVERSION OF AMERICAN TO INTERNATIONAL SYSTEM (SI)* UNITS

	To convert from	to	multiply by
LENGTH	ft	meters	0.305
AREA	ft^2	$meters^2$	0.0929
	acres	$meters^2$	4047
VOLUME	ft^3	$meters^3$	0.0283
	gallons	$meters^3$	0.00379
MASS	lb	kilogram	0.454
	tons	megagram	0.907
WEIGHT RATE OF FLOW	10^3 lb/hr	kg/sec	0.126
	tons/day	kg/sec	0.0105
VOL. RATE OF FLOW	gallons/min	$meters^3$/sec	6.309×10^{-5}
	gallons/min	$millimeters^3$/sec	6309
	10^6 gallons/day	$meters^3$/sec	0.0438
ENERGY	Btu	kilojoule (= Newton x meter)	1.055
	kw-hrs	megajoules	3.60
POWER	H.P.	Joules/sec	746
	kw	Joules/sec	1000
	10^6 Btu/hr	kilojoules/sec	293
SPECIFIC ENERGY	Btu/lb	kilojoules/kg	2.324
PRESSURE	lb/in^2	kilopascall (= kilonewton/m^2)	6.895
WATER FOR ENERGY	gal/10^6 Btu	m^3/megajoule	3.592×10^{-6}
HEAT RATE	Btu/kw-hr	Joules/kw-sec	0.293
TEMPERATURE	°F	°K	0.556 (°F + 459.7)
HEAT TRANSFER COEFFICIENT	Btu/hr.ft^2.°F	Joules/sec.m^2.°K	5.674

---

*Standard for Metric Practice, American Society for Testing and Materials, E380-76, 1976.

SECTION 1

INTRODUCTION

1.1 PURPOSE OF THE STUDY

The purpose of this study is to develop strategies and recommend measures to minimize water pollution and consumption by coal conversion complexes. An important part of environmental assessment of large plants to convert coal is the determination of the quantity of water consumed. In this report the determination of water quality is discussed in great detail and water treatment is described in enough detail to show that full recycle of effluent waters is possible.

1.2 ORGANIZATION OF THE REPORT

The report is divided into two parts entitled "Water Quantities" and "Water Quality."

1.3 WATER QUANTITIES

In the first part of the work, water consumption is studied. Brief descriptions and process water balances are given for a wide variety of coal conversion processes. The Lurgi, Bigas, CO_2-Acceptor and Agglomerating Burner processes convert coal to pipeline gas, also called "substitute natural gas" (SNG) which is more than 90 percent methane and is a direct substitute for natural gas in all applications.

The Winkler, Stirred-Bed, Molten Salt and Koppers-Totzek processes convert coal to power gas, also called fuel gas, low-Btu gas or medium-Btu gas. This gas has a higher heating value in the range 150 Btu/scf (for low-Btu gas) to 350 Btu/scf (for medium-Btu gas) compared to more than 920 Btu/scf for pipeline gas. These heating values are too low for the gas to bear the cost of long-distance transmission in pipelines and are made for local use. Natural gas burners can use a medium-Btu gas, but modification or down-rating is needed for the lowest-Btu gases. Low-Btu gas is made using air as the oxidant. Medium-Btu gas requires oxygen to avoid diluting the gas with nitrogen and the investment is higher.

H-Coal and Synthoil processes convert coal to a liquid fuel which may be an ash-free heavy fuel oil sufficiently free of nitrogen and sulfur or, with process changes, may be refinery feed stock. These are processes in which coal is hydrogenated directly with hydrogen, and the plant complex also has a hydrogen production section in which hydrogen is made by reducing water with coal (gasification of coal with oxygen and steam). Hydrogenation always converts some of the coal to light hydrocarbon gas and liquid which may be sold or burnt as plant fuel.

To determine the quantity of water consumed for any conversion process at any site, one must total the water consumed for the following reasons:

Net process water
Water for cooling
Water for mining and land reclamation
Water lost in evaporation, water lost with solids and other uses.

Four processes are described in more detail so that cooling water requirements can be determined; these are the Hygas and Synthane processes for pipeline gas, the Lurgi process to make low-Btu fuel gas which is burnt on site to generate electricity by the combined cycle method and Solvent Refined Coal (SRC). SRC is a low ash, low nitrogen, low sulfur fuel which has a fusion temperature in the range of 350°-450°F.

The choice and economics of evaporative and dry cooling is studied in detail. At three sites (North Dakota, New Mexico and Wyoming) the water needs for mining, coal handling, etc., are analyzed; these quantities are generally dependent on the site, not on the process.

The conditions and results of the detailed studies are summarized on Table 1-1.

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The consumptive water requirements of Part 1 have been calculated on the assumption that no liquid water leaves the plant. Any water clean enough to be sent to a receiving stream is clean enough for use in the plant, so the assumption of no liquid water effluent is economically, as well as environmentally, correct.

1.4 WATER QUALITY AND TREATMENT

In the second part of the report, water treatment for source water, for recycle water and for reuse water is discussed.

Three sites have been chosen for detailed study: 1) in the vicinity of Beulah, North Dakota using lignite coal and water from Lake Sakakawea. This site is regarded as a standard, or basic, example in that water of good quality is assumed to be cheap and available. 2) The four corners area of New Mexico using Navajo subbituminous coal and a brackish ground water. This site is used to study the effect of a brackish, but plentiful, water supply. 3) In the vicinity of Gillette, Wyoming using subbituminous coal. It is at this site that the water supply for a satellite town has been integrated into the coal conversion plant. Town sewage is taken as the main water supply to the plants, and any other water taken in is assumed to be very expensive because it must be brought from a long way away.

SECTION 2

CONCLUSIONS

2.1 WATER CONSUMPTION

Total water consumption depends on the product, on the site and, possibly to a lesser extent, on the process. Details are tabulated in Section 13 and summarized on Table 1-1 and Figure 2-1.

2.2 WATER TREATMENT

Water treatment costs and energy requirements are given in Figure 2-2 and Tables 1-1 and 10-1. They are much less well defined than water consumption quantities, and more study is required. In deriving Figure 2-2, unproven technologies were used; indeed, unproven technologies had to be assumed because an adequate experimental base is not available for most water treatment technologies on these waters.

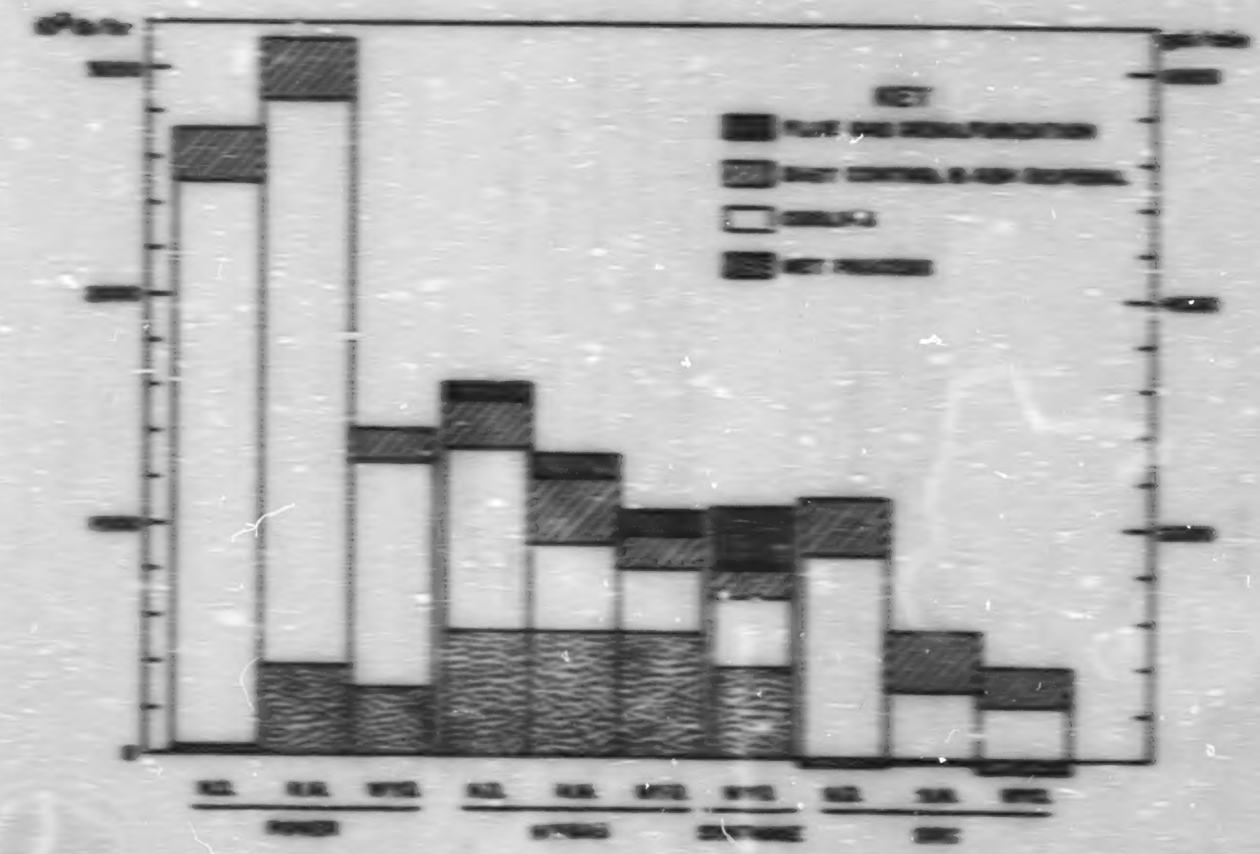


Figure 2-1. Water consumption. (Plant sizes given in Table 2-1.)

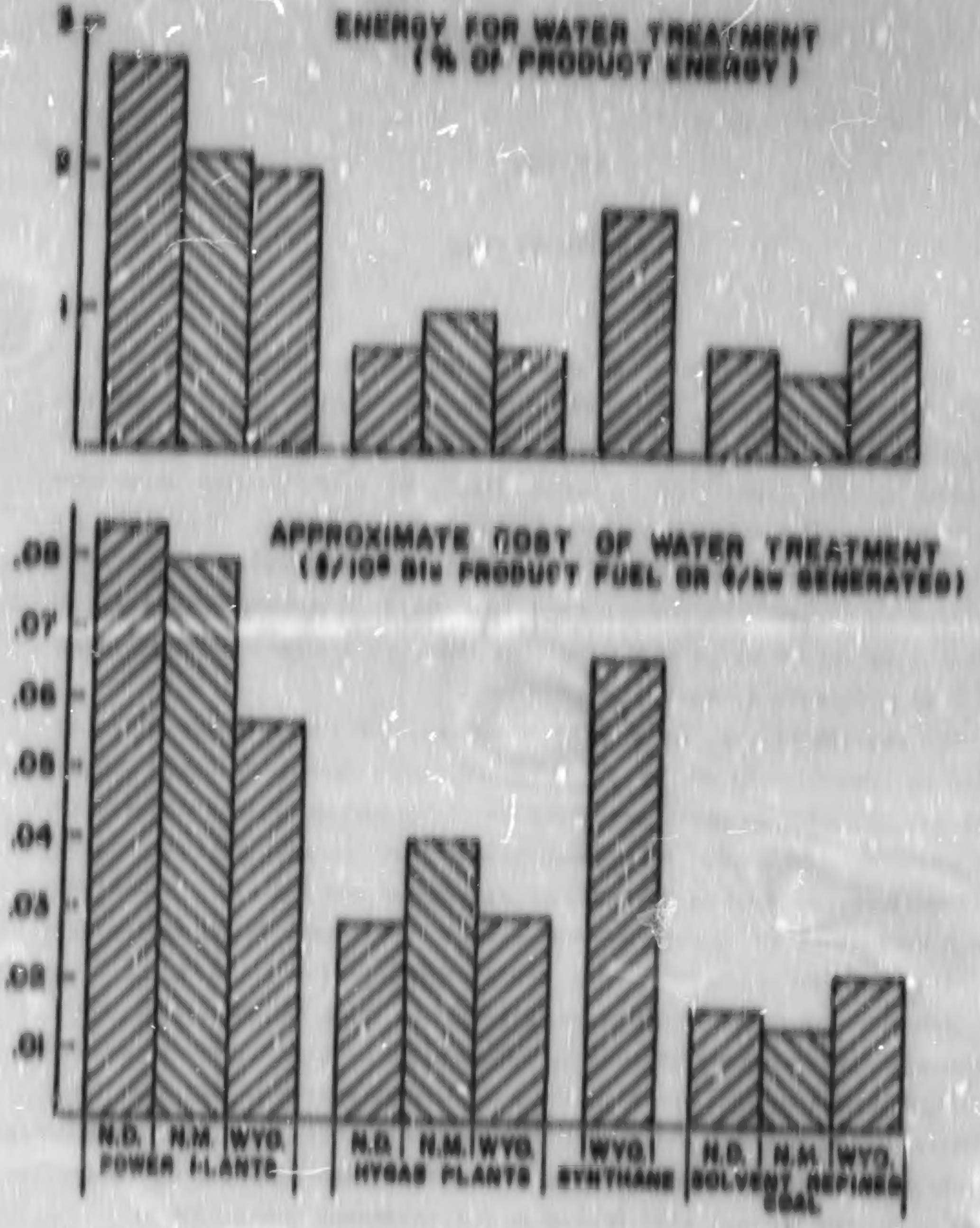


Figure 2-2. Approximate cost and energy requirements of water treatment. (Plant sizes given on Table 1-1.)

SECTION 3

RECOMMENDATIONS

In estimating net water consumptions this study provides a method as well as some answers. We recommend that this method be used when extending the determinations to other processes at other sites. There is a need to know regional total water consumptions when planning water uses, particularly in the Western States, where water is scarce. When totaling the consumptions from many plants to find the regional consumption, considerable accuracy is required for each plant if the absolute error in the total is not to be so large that the total is useless. Attention to detail is necessary to attain accuracy.

The quality of the plant effluent waters, and the response of these waters to treatment is not well understood, and properly designed experiments are needed. In designing treatment experiments it is necessary that real wastewater be used. Analyses available are insufficient to enable the laboratory to produce a simulated wastewater adequately. Furthermore, when a wastewater is to pass through several treatments in series so that the effluent from one treatment is the influent to the next, then all of the treatments must be simultaneously studied. Experimentation on one treatment, isolated from others, is unlikely to be good enough because the composition of the feed water to the isolated treatment is unlikely to be correct. Figure 3-1 shows four simple schemes for reuse of foul process condensate. The cost and procedure for reuse, whether in the cooling tower or in the boiler, will depend on the treatment and cannot be investigated without complete treatment. The design of biological treatment depends on the degree, if any, of ammonia separation and solvent extraction that preceded it; so does the effluent from the biological treatment depend on preceding treatments. Separation of ammonia is the

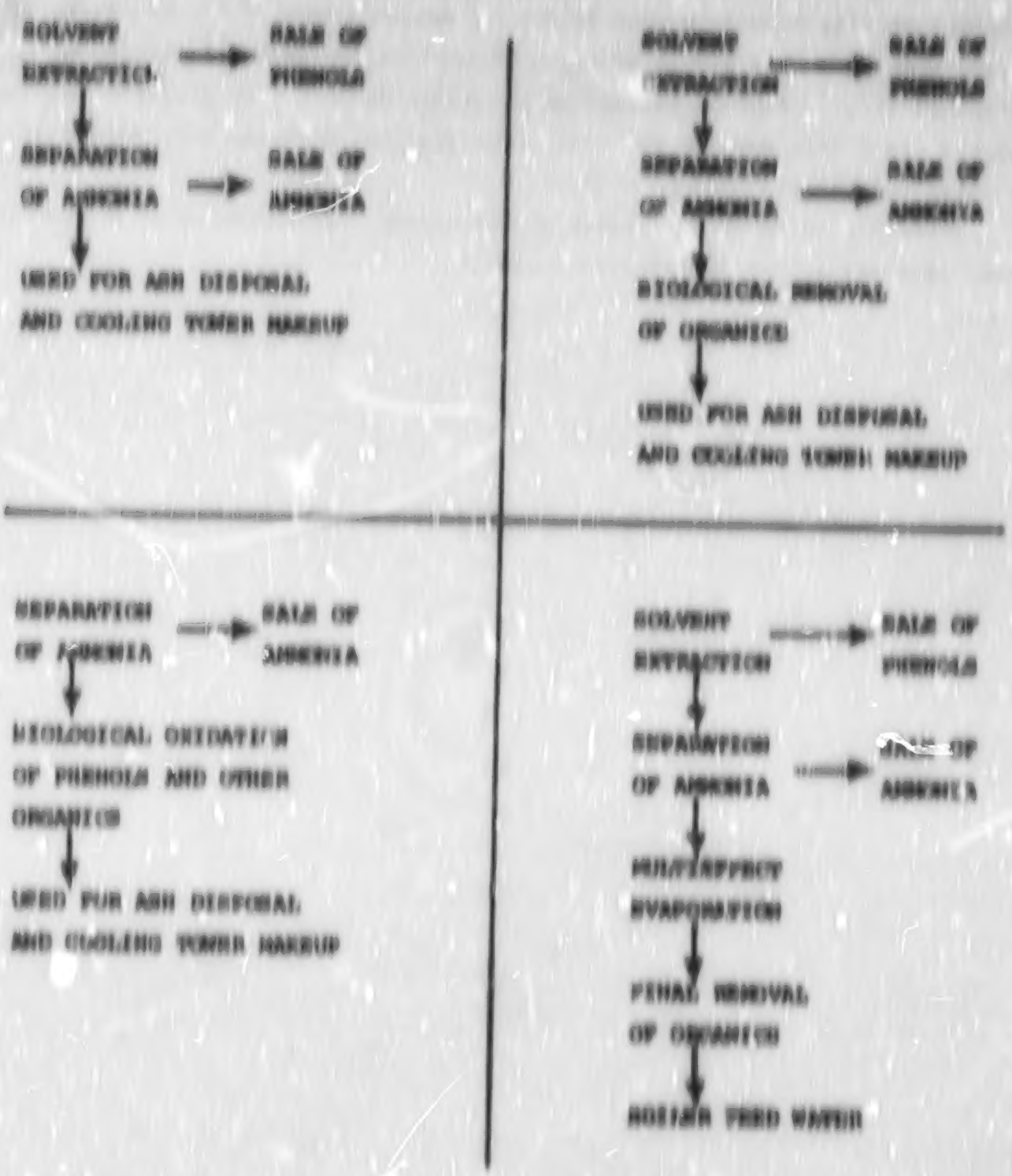

SOLVENT EXTRACTION
SALE OF PHENOLS
SEPARATION OF AMMONIA
SALE OF AMMONIA
USED FOR ASH DISPOSAL AND COOLING TOWER MAKEUP
SOLVENT EXTRACTION
SALE OF PHENOLS
SEPARATION OF AMMONIA
SALE OF AMMONIA
BIOLOGICAL REMOVAL OF ORGANICS
USED FOR ASH DISPOSAL AND COOLING TOWER MAKEUP
SEPARATION OF AMMONIA
SALE OF AMMONIA
BIOLOGICAL OXIDATION OF PHENOLS AND OTHER ORGANICS
USED FOR ASH DISPOSAL AND COOLING TOWER MAKEUP
SOLVENT EXTRACTION
SALE OF PHENOLS
SEPARATION OF AMMONIA
SALE OF AMMONIA
MULTIEFFECT EVAPORATION
FINAL REMOVAL OF ORGANICS
BOILER FEED WATER

Figure 3-1. Schemes for reuse of foul water.

most massive energy-consuming part of the water treatment plant. This energy consumption will depend to some degree on whether phenol has been extracted first; some phenol is always stripped in ammonia separation if it is not extracted first. Solvent extraction is expensive, but sale of extracted phenols can offset some of the cost. The quality, marketability and value of extracted phenols is not known.

These are examples to explain why experiments should be done on complete water treatments, not on individual aspects.

PART 1 - WATER QUANTITIES

SECTION 4

COAL CONVERSION PROCESSES

4.1 INTRODUCTION

In this chapter the quantities of water fed to, and evolved from, various processes to convert coal to other fuels are surveyed where possible. In doing this the literature has been reviewed; new designs have not been made. These water requirements, which we have called process requirements, are not the largest requirements of the plant. However, knowledge of these quantities is important in the design of a water treatment plant because the quality of process water is extreme. Most of the water is fed as steam and so must be of the highest purity. Most of the water evolved is a condensate that has contacted coal, tar, and gas and is particularly dirty.

A diagram of particular plants to make pipeline gas is given for the Hygas/Oxygen process (Figure 5-2) and for the Synthane process (Figure 6-2). Both are described in detail and will be used for the site studies. A simpler and more general diagram showing points of water inflow and outflow is given in Figure 4-1 and used for less detailed descriptions of the Lurgi, Bigas, and CO_2-Acceptor. The Agglomerating Ash process is also described, but there is not enough information to define the water streams.

Pipeline gas is more than 90 percent methane (CH_4). Although some of the hydrogen for the methane is available in combined form in the coal, most of the hydrogen comes from water which is reduced by carbon. A methane output of 250×10^6 standard cubic feet per day contains hydrogen equivalent to 987,000 lb/hr of water (1,976 gpm). In fact, water in excess of that needed for chemical reaction is usually added to the gasifiers to control the

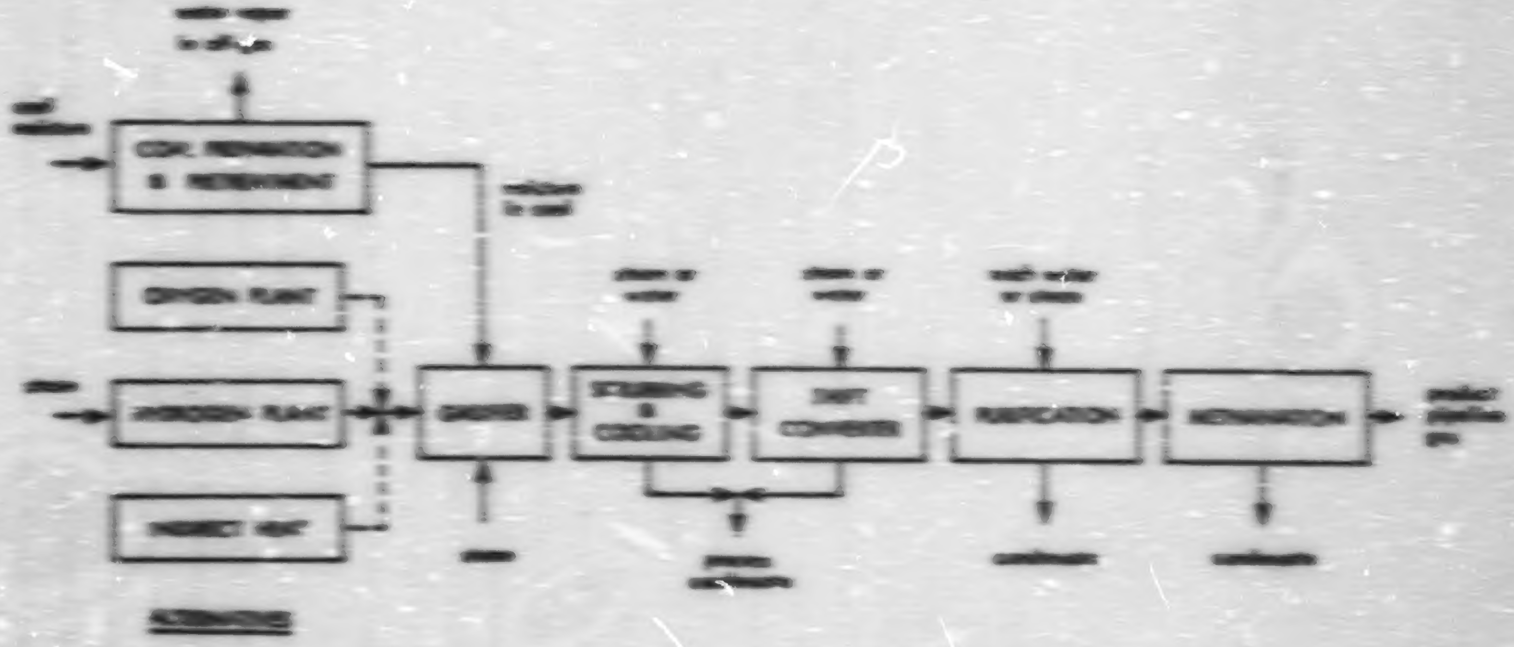

water vapor
to off-gas
coal
moisture
COAL PREPARATION
& PRETREATMENT
moisture
in coal
OXYGEN PLANT
HYDROGEN PLANT
INDIRECT HEAT
ALTERNATIVES
GASIFIER
steam or
water
SCRUBBING
&
COOLING
steam or
water
SHIFT
CONVERTER
wash water
or steam
PURIFICATION
METHANATION
product
pipeline
gas
process
condensate
condensate
condensate

Figure 4-[illegible]. Water streams in a plant to produce pipeline gas from coal.

temperature and moderate the reaction.

The surplus water comes out of the process in several places. Some water is condensed out of the raw gas leaving the gasifier. This water has been called process condensate. In some processes the raw gas is scrubbed with water. This cools the gas and transfers tar, dust, and soluble organic materials from the gas to the water. Cooling also causes condensation of water vapor which left the gasifier. The scrubbing water is circulated and only the surplus water from condensation is removed. The quantity called process condensate is the surplus water actually removed from the process; it is not the quantity of water circulated within the process.

Although many coals contain a high percentage of moisture, this water is not usually available to enter into chemical reaction. Often the coal must be dried before it is fed to the gasifier. Even if coal is not predried, it is usually fed near the top of the reactor where water vaporizes and leaves before it has time to react. A wet coal will usually increase the amount of process condensate but not reduce the steam requirement to the gasifier.

Sometimes additional cooling causes water to condense in the gas purification liquid. Such water must then be boiled out so that the gas purification liquid can be recycled. The quantity of this water is shown in the tables as leaving the purification stage.

Water is formed during the methanation stage and is condensed and knocked out of the product gas. This water is shown in the tables as leaving the methanator.

Figure 4-2 shows the stages in a plant to produce power gas (low-Btu gas) from coal. The processes described are Winkler, Stirred Fixed Bed, Molten Carbonate, Lurgi, and Koppers-Totzek. The Lurgi process is the process chosen for combined-cycle electric power production and is described in more detail in that section. The Koppers-Totzek process is further described as part of the design of the Solvent Refined Coal plant as it is the process chosen to produce hydrogen from the carbonaceous filter residue.

Processes to make clean liquid and solid fuels cannot be shown on a single block diagram. Brief descriptions of the Synthoil and H-Coal processes are given.

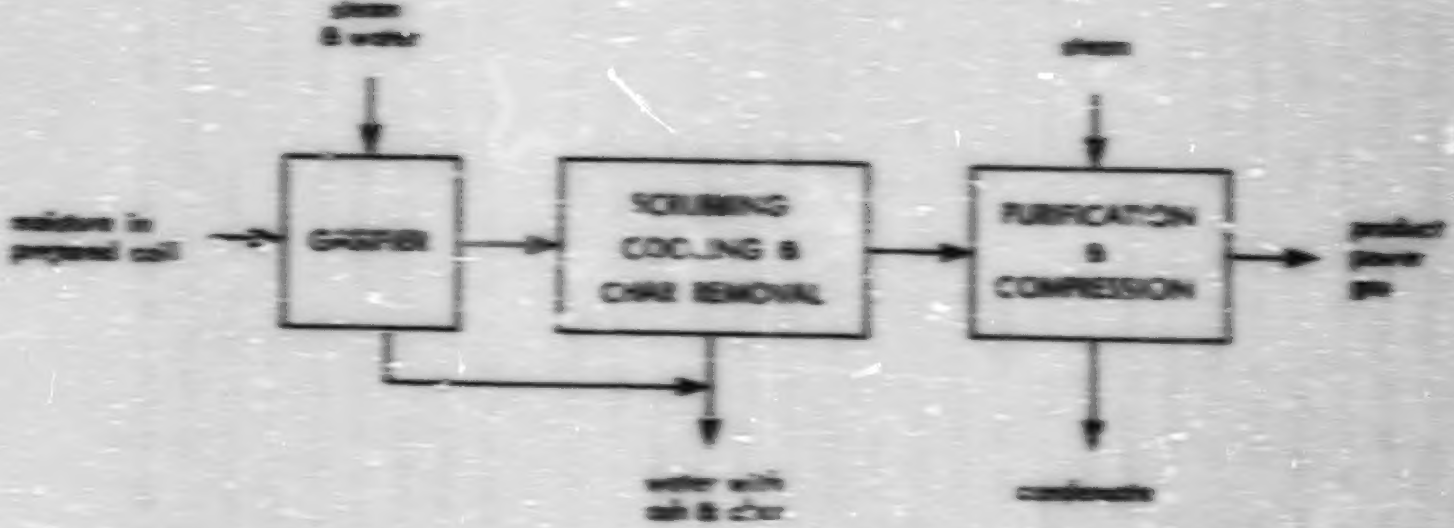

steam
& water
moisture in
prepared coal
GASIFIER
SCRUBBING
COOLING &
CHAR REMOVAL
steam
PURIFICATION
&
COMPRESSION
product
power
gas
water with
ash & char
condensate

Figure 4-2. Water streams in a plant to produce power gas from coal.

4.2 LURGI PROCESS

Brief descriptions of the Lurgi and many other processes will be found in Reference 1. The Lurgi commercial plant operation experience is given in References 2-5. At least four full-sized commercial plants have been described: the Wesco plant using Navajo coal in the "Four Corners" area of New Mexico;[6-10] the El Paso plant in the same region;[11-14] the Wyoming-Rochelle plant in Campbell and Converse counties Wyoming,[15] and the Michigan-Wisconsin plant using lignite in Mercer county, North Dakota.[16]

The Lurgi gasifier shown in Figure 4-3 consists of a number of chambers stacked vertically. From top to bottom they are: coal bunker, coal lock chamber, water jacketed gas producer chamber, ash lock chamber and ash quench chamber. Coal crushed and screened to 1.5 to 0.19 inch flows through the lock chamber to the pressurized reactor maintained at 350 to 450 psi. Steam and oxygen are introduced through a revolving grate at the bottom of the reactor.

The moving bed of coal, which is the volume between the inlet and outlet grates, has several distinct zones. Devolatilization occurs at the top and gasification begins lower down where the temperature reaches 1150°F and 1400°F. The minimum residence time of coal at the desired temperature level of 1400°F to 1600°F is about one hour. The bottom of the coal bed is the combustion zone in which about 14 percent of the coal fed to the gasifier is burned with oxygen to supply heat for the endothermic gasification reaction. Solid ash is removed through the ash lock chamber at the bottom.

The crude gas leaves the gasifier at temperatures between 700°F and 1100°F, depending upon the type of coal. It contains carbonization products such as tar, oil, naphtha, phenols, ammonia, etc., and traces of coal and ash dust. Quenching with circulating water moves the contaminants from the gas into the water. A portion of the cooled crude gas goes to a shift conversion reactor where CO and H_2O are catalytically converted to H_2 and CO_2 so that the H_2/CO ratio of the mixed gas is adjusted to greater than 3 suitable for the methanation step. After shift conversion the acid gases are usually removed by the Rectisol process, although other acid gas removal processes are feasible. Finally, the purified gas passes through the methanation stage consisting of fixed bed reactors with pelleted reduced nickel type catalysts.

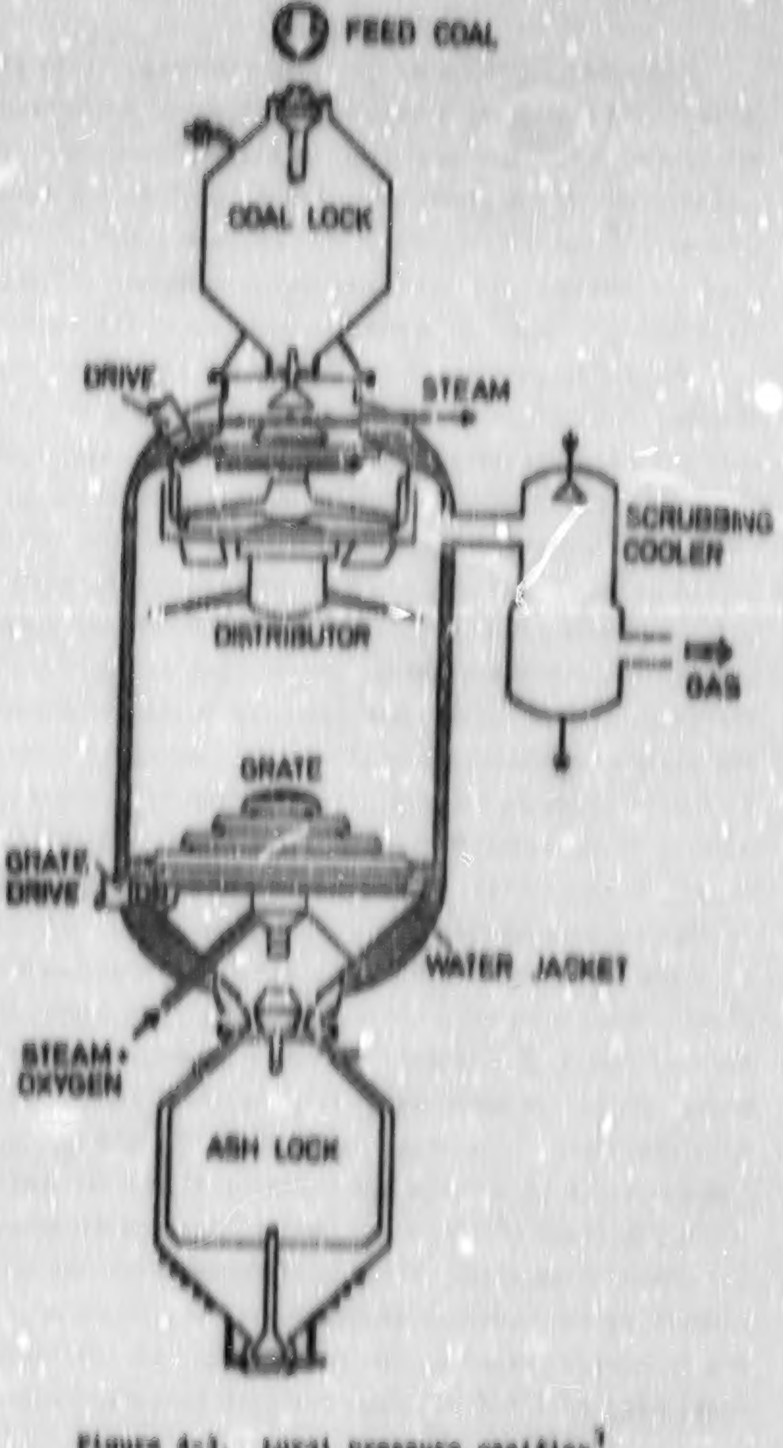

FEED COAL
COAL LOCK
DRIVE
STEAM
SCRUBBING COOLER
DISTRIBUTOR
GAS
GRATE
GRATE DRIVE
WATER JACKET
STEAM + OXYGEN
ASH LOCK

Figure 4-3. Lurgi pressure gasifier[7].

Table 4-1 compares some of the operating conditions for the four commercial designs studied. For these designs hydrogen balances are given in Table 4-2. This table shows the range of variation to be expected between designs for a chosen process. All the numbers are scaled to a production rate of 250 × 10^6 SCF per day. Table 4-2 shows clearly that moisture in the coal does not enter into reaction but is evolved as condensate. Coal moisture is the major difference among the plants shown on Table 4-2. The major difference among the plants shown on Table 4-1 is cooling water. The El Paso and Wesco plants, while both on the same site and using the same coal, differ. For El Paso, coal is gasified to produce a low sulfur fuel gas to provide driving energy for the plant. Many of the drive turbines are gas turbines not requiring steam condensers. For Wesco, washed coal is burned to raise steam to drive the plant. The needs for cooling water are not, therefore, comparable in the two plants. (The needs for cooling water are discussed more fully in Section 10.) At both plants, treated dirty condensate supplies all the cooling water makeup and a lot of direct air cooling is used. Cooling water is evaporated to remove about 26 percent of the heat in the feed coal not recovered as product gas or byproducts. At the Michigan-Wisconsin plant in North Dakota, cooling water is evaporated to remove about 46 percent of the heat in the feed coal not recovered as product gas or byproducts. Even more water is evaporated than is recovered as condensate. This is the designer's choice, it is not a necessity.

4.3 BIGAS PROCESS

The Bigas process for the production of pipeline gas from coal is under development by Bituminous Coal Research, Inc., under the sponsorship of the Office of Coal Research and the American Gas Association. More detailed descriptions of this process can be found in References 17 to 23. Development work has proceeded from batch-type experiments to a fully integrated 5 ton/hr gasification pilot plant at Homer City, Pennsylvania currently under construction.

Coal will be received from the mine and wet ground until 70 percent of it will pass through a 200 mesh screen. The coal will be then pumped to

TABLE 4-1. LURGI PROCESS DESIGNS

All plants scaled to 250 x 10^6 scf/day.

		El Paso	Wesco	Michigan-Wisconsin	Wyoming-Rochelle
GASIFIER INFORMATION					
Coal feed	10^3 lb/hr	1683	1823	2161	1750
Coal feed	10^9 Btu/hr	14.6	15.1	14.7	17.8
Oxygen feed	10^3 lb/hr	400	473	426	450
Oxygen feed	lb/lb (carbon + hyd.)	0.44	0.48	0.46	0.44
Steam and bfw	lb/lb (carbon + hyd.)	1.7	1.8	2.4	(1)
THERMAL EFFICIENCY, %		~ 67	~ 68	~ 65	
$\frac{\text{HHV (product gas + by-products)}}{\text{HHV coal feed}}$					
COOLING TOWERS					
Water evaporated	10^3 lb/hr	1217	880	2849	

---

(1) Not Known

TABLE 4-2. WATER EQUIVALENT HYDROGEN BALANCES FOR LURGI PROCESSES

All plants scaled to 250 x 10^6 scf/day.

Units: 10^3 lb/hr.

	El Paso	Wesco	Michigan-Wisconsin	Wyoming-Rochelle
IN				
Moisture in as-received coal	273	236	778	411
Water equivalent of hydrogen in coal	545	580	529	630
Steam and boiler feed water (2)	1635	1991	∿ 2226	(1)
	2453	2807	3533	
OUT				
Dirty condensate from scrubber, shift reactor and purification (3)	1084	1488	1997	∿ 1870
Clean condensate from methanation (3)	274	311	∿ 290	∿ 290
Water equivalent of hydrogen in Naptha and other byproducts	206	40	88	∿ 90
Water equivalent of hydrogen in product gas	943	960	963	∿ 960
	2507	2799	3338	

---

(1) Not known
(2) Clean water inflow
(3) Effluent water

(continued)

TABLE 4-2. (continued)

Units: gals. water/10^6 Btu in product gas.

	El Paso	Wesco	Michigan-Wisconsin	Wyoming-Coalgasco
IN				
Moisture in coal	3.3	2.7	9.2	~6.9
Water equivalent of hydrogen in coal	6.6	6.9	6.2	~7.5
Steam and boiler feed water	19.7	23.3	~26.2	
	29.6	32.9	41.6	
OUT				
Dirty condensate from scrubber, shift reactor and purification	13.1	17.4	23.5	~22.1
Clean condensate from methanation	3.3	3.7	~3.4	~3.4
Water equivalent of hydrogen in naptha and other byproducts	2.5	0.5	1.0	~1.0
Water equivalent of hydrogen in product gas	11.5	11.3	11.3	~11.4
	30.4	32.9	39.2	

pressurized storage hoppers in a water slurry of up to 50 percent coal. The water used for slurrying will be vaporized in the pressurized storage and may be passed on to the shift converter. Figure 4-4 shows one conceptual design.

The Bigas reactor is a two-zone, refractory-lined and water-cooled gasifier operating at approximately 1200 psig (Figures 4-5 and 4-6). The coal and steam enter the upper section (Zone 2) of the gasifier through four upward-directed, concentric injection nozzles which produce an entrained flow. The feed coal is heated very rapidly by the hot synthesis gas and steam rising from Zone 1 and in a matter of a few milliseconds is devolatilized to produce methane plus a highly reactive carbon char. Some 50 percent of the product methane is produced in this stage.

The coal residence time in Zone 2 is 6 to 10 seconds with an upward gas velocity of about 5 ft/sec. The gases with entrained char leave Zone 2 at 1800°F. In the pilot plant water will be added to the leaving gases which will vaporize and cool the stream to about 900°F. A waste heat boiler might be possible. The gases then pass to cyclone separators. The gases leaving the separators are further quenched and washed before going to the shift converter at about 650°F.

The char is separated and drained back to Zone 1 of the gasifier where it reacts with steam and oxygen. In Zone 1 the temperature is 2800°F and the carbon is gasified to synthesis gas and the ash residue forms a molten slag. The Zone 1 coal residence time is about 2 seconds and the upward gas velocity is about 6 ft/sec. As a result of the short residence times the capacity of the Bigas gasifier is very much higher than that of a fixed bed gasifier. The hot synthesis gas with entrained char passes upwards to Zone 2. The molten slag is dropped out of Zone 1 and quenched.

Steam is added to the raw gas to adjust the steam-to-dry-gas mole ratio to unity. The gas then enters an adiabatic shift converter having a fixed-bed catalyst and the H_2/CO mole ratio is shifted from about 1:1 to about 3:1, a ratio suitable for methanation. The hot exit gas is then cooled down through a series of heat exchangers and process condensate, formed on cooling, is discharged. Process condensate water is low in organic material because of the high temperature of the gasification.

The pilot plant will use the Selexol process to remove acid gases.

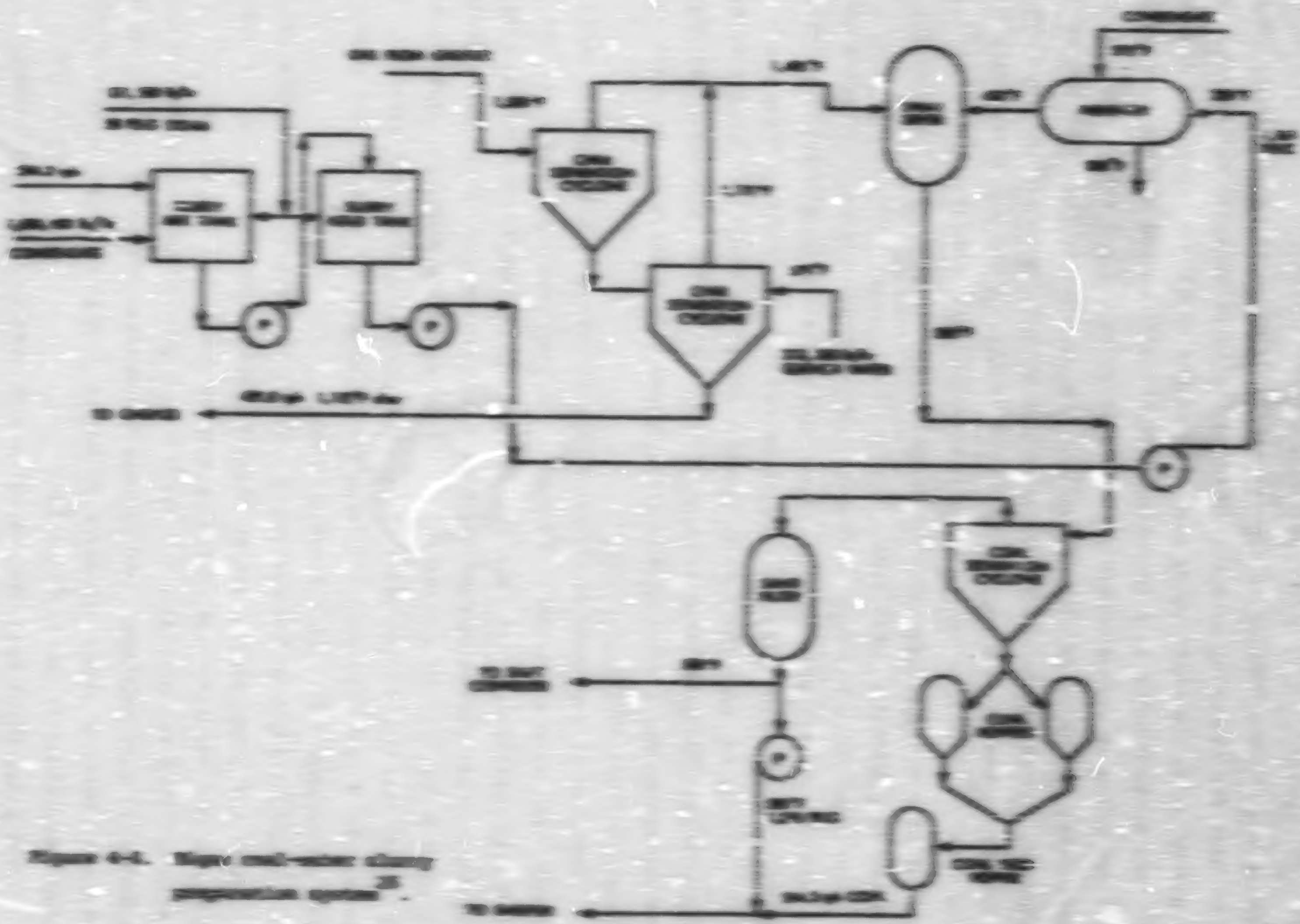


Figure 4-4. Typical coal-water slurry preparation system[25].

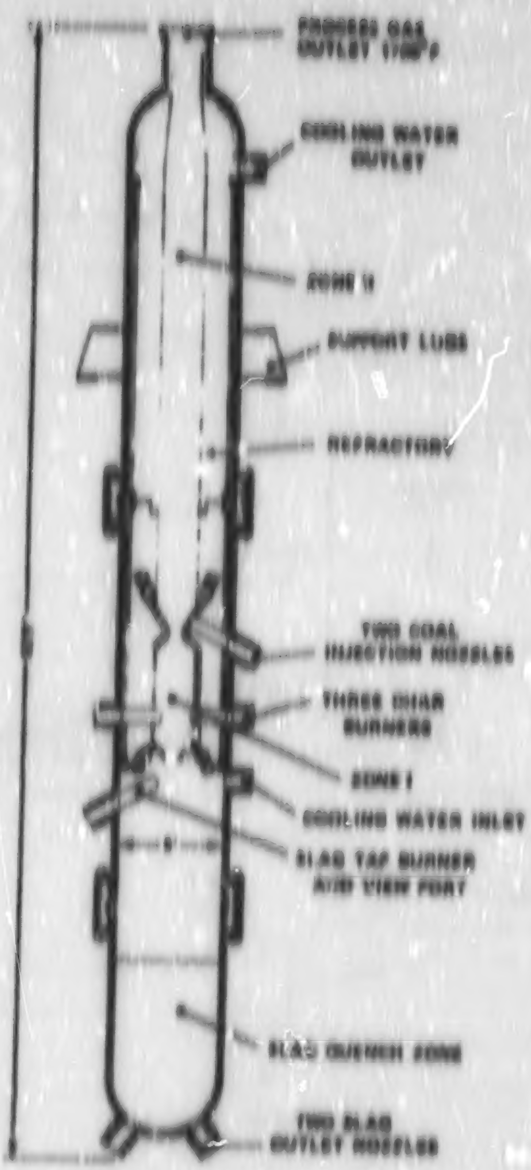

PROCESS GAS OUTLET (TOP)
COOLING WATER OUTLET
ZONE II
SUPPORT LUGS
REFRACTORY
TWO COAL INJECTION NOZZLES
THREE CHAR BURNERS
ZONE I
COOLING WATER INLET
SLAG TAP BURNER AND VIEW PORT
SLAG QUENCH ZONE
TWO SLAG OUTLET NOZZLES

Figure 4-5. Design features of a Bigas process reactor[33].

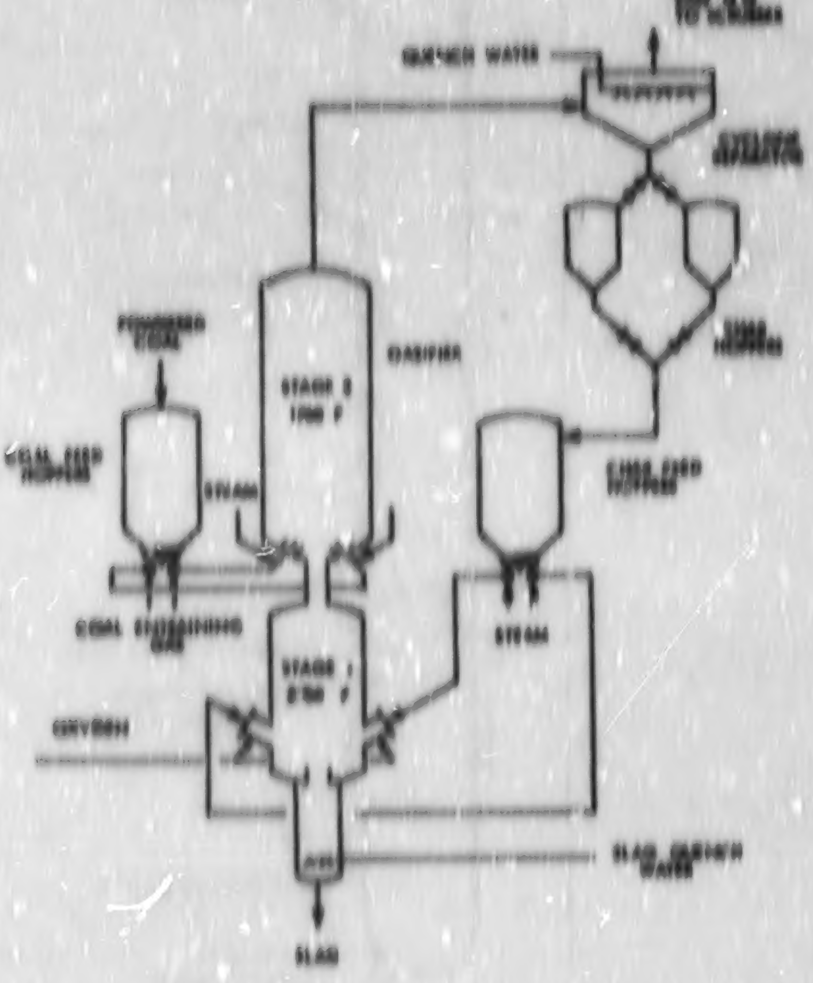

RAW GAS TO SCRUBBER
QUENCH WATER
CYCLONE SEPARATOR
CHAR HOPPERS
POWDERED COAL
GASIFIER
STAGE 2
COAL FEED HOPPER
STEAM
CHAR FEED HOPPER
COAL DISTRIBUTING RING
STEAM
STAGE 1
OXYGEN
SLAG QUENCH WATER
SLAG

Figure 4-6. Bigas gasifier.

Bituminous Coal Research is developing a high temperature fluidized bed methanator,[21] in which 90 percent or more of the carbon monoxide is converted in a single pass. The final conversion of carbon monoxide will occur in a standard fixed-bed cleanup methanator.

In Table 4-2 is presented a water equivalent hydrogen balance of the relevant process streams for a Bigas commercial gasification plant using Kentucky coal. The quench water may enter the system in several places as shown in Figure 4-6. Piston feeding of coal used in the Air Products and Chemicals, Inc. design[18] is superseded, the thermodynamical feasibility of using a slurry feed system having been established[24] and incorporated into the pilot plant designs.[19] Table 4-3 presents a similar water equivalent hydrogen balance using a Montana subbituminous coal-water slurry feed system design made in 1974.

4.4 CO_2-ACCEPTOR PROCESS

The CO_2-Acceptor fluidized-bed process to convert lignite or subbituminous coal to pipeline gas is being developed by Conoco Coal Development Co. The basic feature of this process is to provide heat for the endothermic coal gasification reaction by reacting CO_2 and CaO. The lime-bearing material dolomite is the acceptor of the CO_2-Acceptor process. Currently, a demonstration program sponsored by ERDA is under way in a 40-ton per day pilot plant located in Rapid City, South Dakota. More information can be found in References 26-30.

Raw lignite is crushed to approximately 1/4 - 1/8 inch in a hot-gas-swept impact mill and lifted with hot flue gas to the preheater. The lignite, originally about 30 percent moisture, enters the preheater with about 5 percent moisture. The preheater in a large plant would be fluidized with flue gas for energy conservation. The preheater operates at atmospheric pressure and 400-500°F. Pyrolysis of the coal does not occur. In the pilot plant the residence time in the preheater is 16 hours.

Preheated lignite is fed to the bottom of the char phase of the fluid bed gasifier via lock hoppers (Figure 4-7). Steam is introduced and reacts with the lignite. The gasifier and regenerator operate at 150 psig. Hot dolomite,

TABLE 4-1. WATER EQUIVALENT HYDROGEN BALANCES FOR BIGAS PROCESS

Basis: 250 SCF/day

Units: 10^3 lb/hr

	Kentucky Coal[10]	Montana Subbituminous[25]
PROCESS INFORMATION		
Coal feed to gasifier at 1.3% moisture	846	1089
HYDROGEN BALANCE		
IN		
Moisture in coal	17	14
Water equivalent of hydrogen in coal	428	446
Steam fed	510	692
Water to gas quench	1256	
Water to slurry preparation		1089
Water to char quench	___	213
	2216	2454
OUT		
Condensate from shift conversion and purification	996	1269
Clean condensate from methanation	342	206
Water equivalent of material removed in purification	26	4
Water equivalent of hydrogen in product gas	841	937
	2205	2416

(continued)

TABLE 4-3. (continued)

Units: gallons/10^6 Btu

	Kentucky Coal	Montana Subbituminous
IN		
Moisture in coal	0.1	0.2
Water equivalent of hydrogen in coal	5.2	5.4
Steam fed	6.3	8.4
Water to gas quench	15.3	
Water to slurry preparation		13.2
Water to char quench	____	2.6
	26.9	29.8
OUT		
Condensate from shift conversion and purification	12.2	15.4
Clean condensate from methanation	3.0	2.5
Water equivalent of material removed in purification	0.3	0.1
Water equivalent of hydrogen in product gas	11.5	11.4
	27.0	29.4

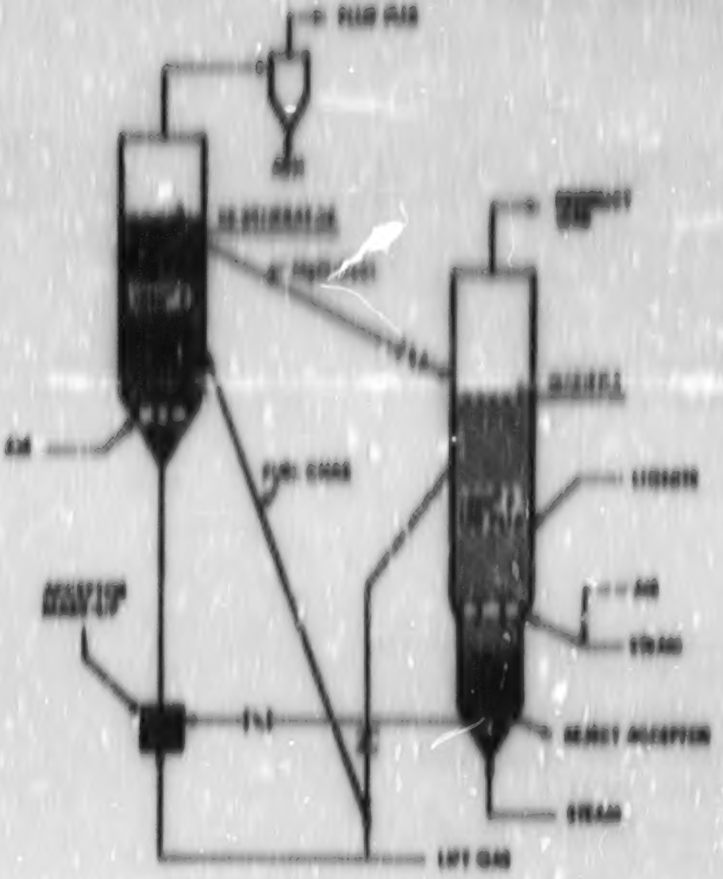

FLUE GAS
ASH
REGENERATOR
PRODUCT GAS
FUEL CHAR
GASIFIER
LIGNITE
AIR
AIR
STEAM
ACCEPTOR MAKE-UP
REJECT ACCEPTOR
STEAM
LIFT GAS

Figure 4-7. CO_2-Acceptor gasifier block diagram.

of acceptor from the regenerator, showers through the lignite bed absorbing CO_2 which drives the water-gas shift reaction to completion so that the gas leaving the gasifier is rich in hydrogen. The absorption of CO_2 also supplies heat to maintain the gasifier at 1480-1520°F or better.

Acceptor accumulates at the bottom of the gasifier where it flows out. Char (about 33 percent of the carbon in the feed coal) is allowed to flow from the top of the gasifier. Separate exit points for acceptor and char allow a concentration ratio of char to acceptor in the gasifier that is not the same as the ratio of the circulation rates. In the pilot plant char is withdrawn at 600 lb/hr and acceptor is withdrawn at 1100 lb/hr, but the weight ratio of char to acceptor in the gasifier is much higher than 6:11. The residence time of acceptor in the gasifier is less than the residence time of char. The char residence time is sufficiently long that phenols, tars and oils are not formed.

In the pilot plant acceptor is lifted to the regenerator by flue gas. Air may be used if the lift line is made resistant to corrosion. Fresh acceptor is added and used acceptor is withdrawn at a rate required to maintain the activity of the acceptor. Char is lifted to the regenerator with nitrogen in the pilot plant. Flue gas may also be used. In the regenerator air is added to burn the char and raise the temperature to 1840-1860°F. This reverses the acceptor reaction and drives off CO_2. Ash is elutriated from the regenerator and recovered in cyclones from which it is released via lock hoppers. The ash contains less than 10 percent carbon.

The gas leaving the gasifier contains, as H_2S, 10-20 percent of the sulfur in the feed coal. The balance of the sulfur, 80-90 percent, is converted to CaS. The ratio of H_2 to CO exceeds 3:1 and a shift reactor is not required.

Table 4-4 presents a water equivalent hydrogen balance scaled to 250×10^6 SCF/day of pipeline gas from the conceptual design for 260×10^6 SCF/day.[20]

4.5 AGGLOMERATING BURNER-GASIFICATION PROCESS

The Agglomerating Burner-Gasification process as described by

TABLE 4-4. WATER EQUIVALENT HYDROGEN BALANCE FOR THE CO_2-ACCEPTOR PROCESS

Coal feed: 2,240,865 lb/hr of North Dakota lignite as received (33.67 wt.% of moisture). 1,281,215 lb/hr of preheated, moisture-free lignite fed to the gasifier (heating value 11,120 Btu/lb).

Product pipeline gas: 250 x 10^6 SCF/day at heating value of 953 Btu/SCF.

	10^3 lb/hr	gals/10^6 Btu
IN		
Water equivalent of hydrogen in preheated lignite to devolatilizer	462	5.6
Steam to gasifier	1035	12.5
	1497	18.1
OUT		
Water vapor in flue gas from regenerator	23	0.3
Process condensate from cooling and spraying	155	1.9
Process condensate from purification	115	1.4
Condensate from methanation	256	3.1
Water equiv. of hydrogen from purification (H_2S)	1	-
Water equiv. of hydrogen in product gas	918	11.1
	1468	17.8

Battelle/Union Carbide[31] is a pressurized, two-stage, fluidized-bed system involving combustion of coal or char in one fluidized bed and the steam gasification of coal in a separate fluidized bed. The heat for the gasification reactions is provided by circulation of ash from the burner to the gasifier. The self-agglomerating method of fluidized-bed combustion, a key feature to the process, consists of burner operation conditions which cause the ash in the coal to agglomerate into free-flowing, inert solid pellets.

Initial development of this process was conducted by Battelle in the early and mid-sixties under sponsorship of Union Carbide. Current objectives include a large-scale development at higher-than-atmospheric pressure. A 25-ton-coal/day Process Development Unit is presently under construction at West Jefferson, Ohio. It will produce between 600,000 and 1,800,000 SCF/day of synthesis gas. The gasification section of the PDU will operate under about 100 psig of pressure.

The burner-gasification section is shown in Figure 4-8. For the Eastern bituminous coal to be used in the PDU, the burner will operate at 2050°F and the gasifier at about 1600°F.

Crushed coal (minus 100 mesh) and conveying air will enter the burner by a pipe which passes through, and is flush with, the surface of the air distributor plate. Additional air will enter from below the distributor plate.

During initial operation the fluidized bed in the burner will be maintained below the point where the diameter increases. Thus, agglomerated ash particles will overflow the burner and be continuously transferred to the gasifier by means of a steam lift.

Coal (minus 8 plus 100 mesh) will enter the gasifier on the same horizontal plane as the feed location for ash agglomerates. Superheated steam will enter the gasifier below and above the fluidized-bed distributor plate. There will be a net downward flow of agglomerated ash particles through the gasifier. In passing through, they will transfer a portion of their sensible heat to support the gasification reactions. Ash agglomerates will be continuously stripped of carbon by the upward flow of steam and will be then continuously returned to the burner by means of an air lift for reheating. In passing through the gasifier, the ash agglomerate temperature drops from 2000°F to 1500-1600°F. Ash agglomerates will be removed from the loop at a rate equa-

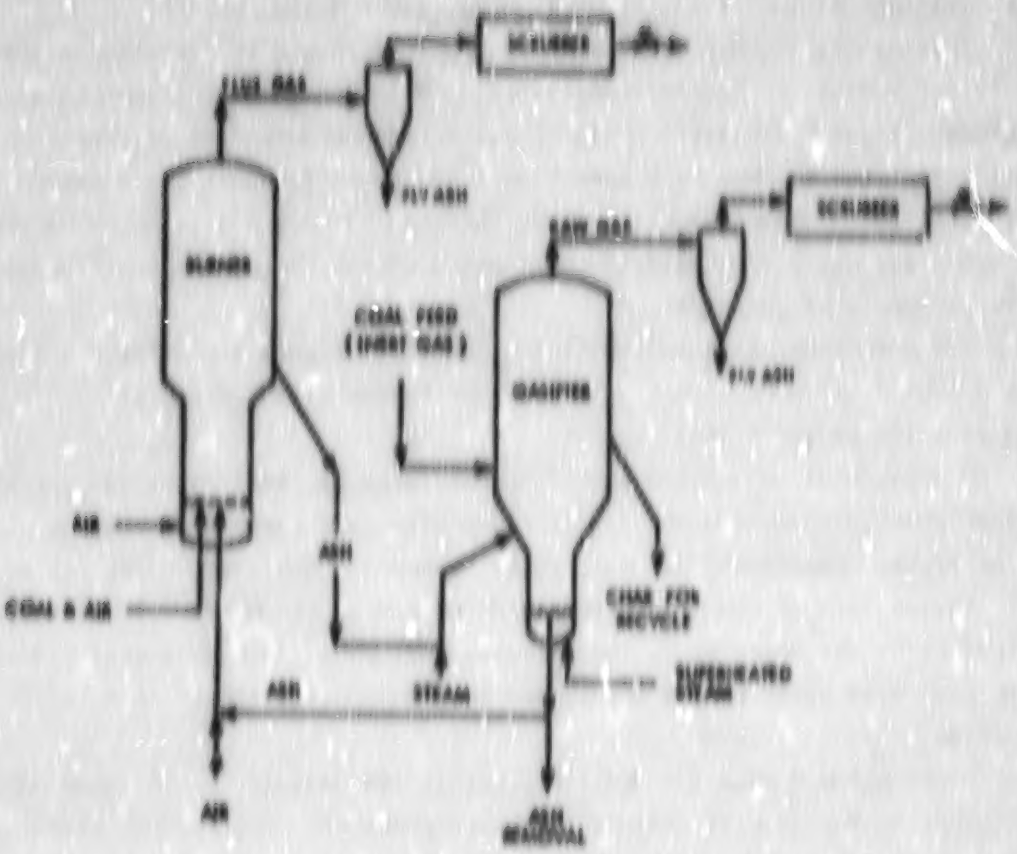

SCRUBBER
FLUE GAS
FLY ASH
SCRUBBER
RAW GAS
BURNER
COAL FEED
(INERT GAS)
GASIFIER
FLY ASH
AIR
ASH
COAL & AIR
CHAR FOR
RECYCLE
SUPERHEATED
STEAM
ASH
STEAM
AIR
ASH
REMOVAL

Figure 4-6. Burner-gasifier feed and circulation system for Agglomerating Burner gasification process[71].

to that of the ash in the fuel fed to the system.

No material balance information has been published.

4.6 WINKLER PROCESS

The Winkler process to produce low- or medium-Btu power gas has been in operation since the twenties. The heating value of the product gas depends on whether air or oxygen is used as the gasifying medium. The main difference between the oxygen blown Winkler process and the various processes described to produce high-Btu pipeline gas is the absence of a shift converter and a methanation stage. Details of the Winkler process can be found in References 32 and 33.

Crushed coal (smaller than 3/8 inch) is fed to the gasifier (Figure 4-9) through a variable speed screw feeder. Operating experience shows that drying the coal before gasification is not necessary so long as the surface of the coal is not wet (approximately 10 percent moisture content or less). In the fluidized bed of the Winkler gasifier, the coal particles react with oxygen (or air if low-Btu gas is desired) and steam resulting in a gas rich in hydrogen and carbon monoxide. The gasification temperature is in the range of 1480 to 1850°F depending on the reactivity of the coal used. The pressure is about one to three atmospheres. Unreacted carbon entrained in the gas is gasified with secondary oxygen and steam in the space above the fluidized bed, so that the maximum temperature occurs above the fluidized bed. This helps to decrease the production of tars and oils.

To prevent molten ash from forming deposits blocking the gas exit duct, the gas is cooled in a radiant boiler immediately above the gasification zone. About 70 percent of the ash is carried over by gas and 30 percent is removed from the bottom of the gasifier. After the sensible heat of the raw gas leaving the gasifier is recovered, fly ash and char are removed by cyclones followed by a wet scrubber and, finally, an electrostatic precipitator.

Purification (desulfurization) of the raw gas may be achieved by any of the commercially available acid gas removal systems. As examples, a combination of COS hydrolysis and Alkazid absorption is recommended,[33] as is the Stretford system.[32]

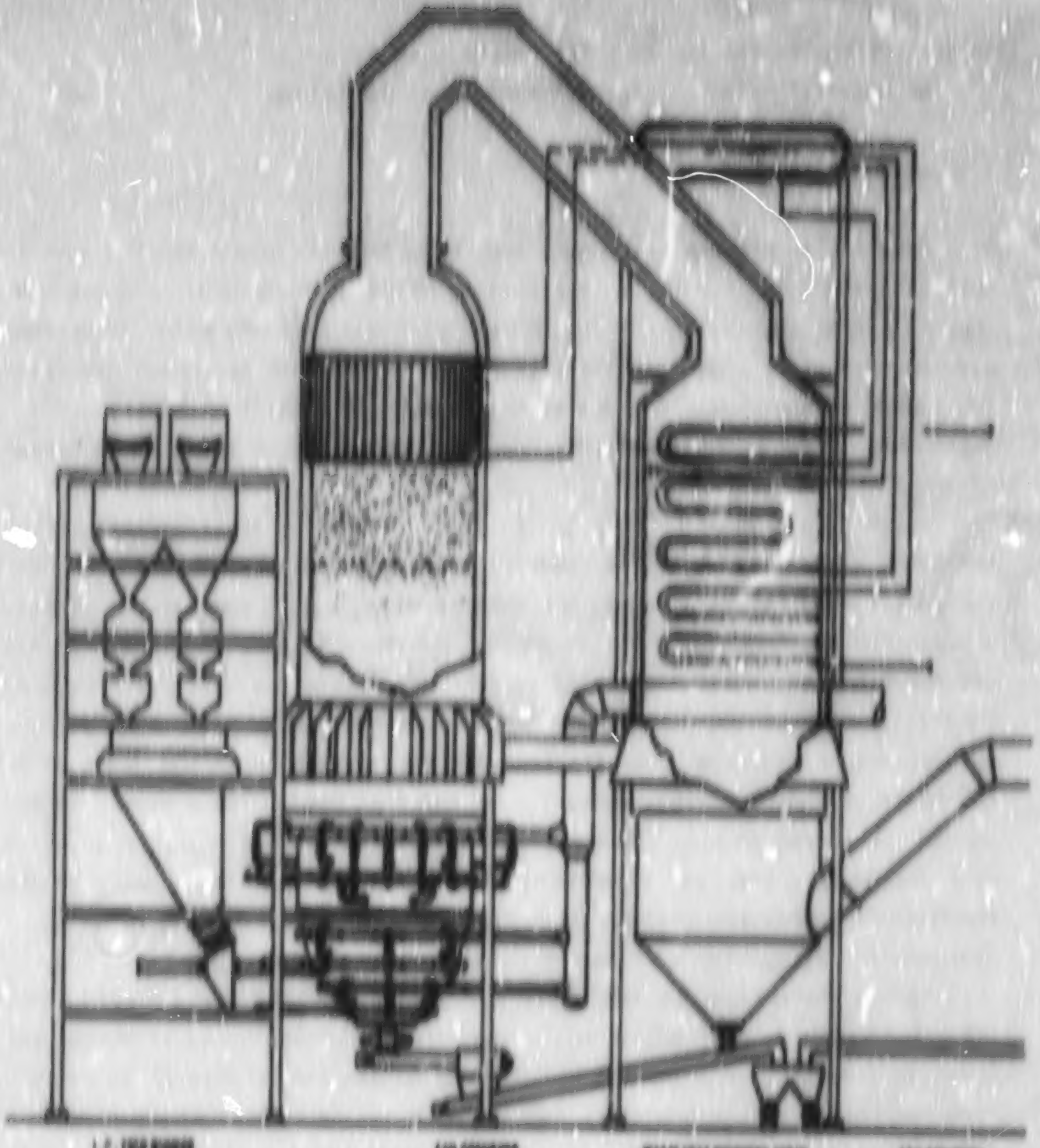

L.P. FEED BUNKER
LOCK HOPPERS
H.P. FEED BUNKER
FEED SCREWS
GASIFIER
ASH CONVEYOR
ROTARY LOCKS

Figure 4-9 Winkler gasifier and heat recovery system[34].

Table 4-5 presents a process water equivalent hydrogen balance for an integrated oxygen-blown Winkler process. Also in Table 4-5 is a similar balance of relevant process streams for an integrated air-blown Winkler process. The tables are based on the preliminary process designs for production of 10.5×10^6 SCF/day of medium-Btu gas and 23.4×10^6 SCF/day of low-Btu gas[23] and we expressed the results in gals/10^6 Btu of product gas. The use of oxygen requires more steam to the gasifier to control the reaction. One third of the extra steam reacts and two thirds is recovered as dirty condensate.

4.7 THE STIRRED-BED PROCESS

The Stirred-Bed Producer is under development at the Bureau of Mines in Morgantown, West Virginia.[35-38] Figure 4-10 shows the pilot plant producer. The producer operates at about 105 psi. In a typical run, coal having the analysis shown on Table 4-6 is fed to the reactor at a rate of 1800 lb/hr. Air and superheated steam were introduced below the grid and passed upwards through the descending coal producing the gas which is withdrawn through an off-take in the top cover. 0.4 lb steam is used per pound of coal (and 3.6 lb of air). The temperature at the exit is held to about 1000°F by the steam/coal/air ratio. Gas having the composition of Table 4-6 was produced at a rate of 77,700 SCF/hr.

In the pilot plant, deep continuous stirring is provided within the producer by a water-cooled stirrer equipped for compound motion that is a horizontal rotation and vertical reciprocation. The stirrer prevents caking and promotes good gas to solid contact. Pressure in the gasifier is maintained by the resistance to gas flow through the off-take line containing a primary orifice of diameter 1.067 inches and a secondary orifice of .800 inch diameter. Located between the two orifices there is a cyclone separator to remove part of the dust entrained in the gas.

For startup, anthracite is used to avoid depositing tar in the cold system. Steam flow is started and then air flow increased slowly. Untreated, bituminous, crushed coal feed is introduced when the gas reaches an off-take temperature of 1000°F. Approximately four hours is required for the anthracite to burn out and be completely replaced by a bituminous bed.[35]

TABLE 4-5. WATER EQUIVALENT HYDROGEN BALANCES FOR THE WINKLER PROCESS (KENTUCKY COAL)

	mols/10^6 Btu of product gas	
	oxygen blown	air blown
IN		
Moisture in coal	0.7	0.6
Water equiv. of hydrogen in coal	4.7	5.6
Steam to gasifier	12.1	5.3
Process water to gasifier	1.0	0.8
	18.5	12.4
OUT		
Settler waste water from char removal	7.6	3.7
Moisture in wet char from char removal	0.7	0.6
Water vapor in vent gas from char removal	0.1	0.1
Water equiv. of hydrogen in product gas	10.1	8.1
	18.5	12.5

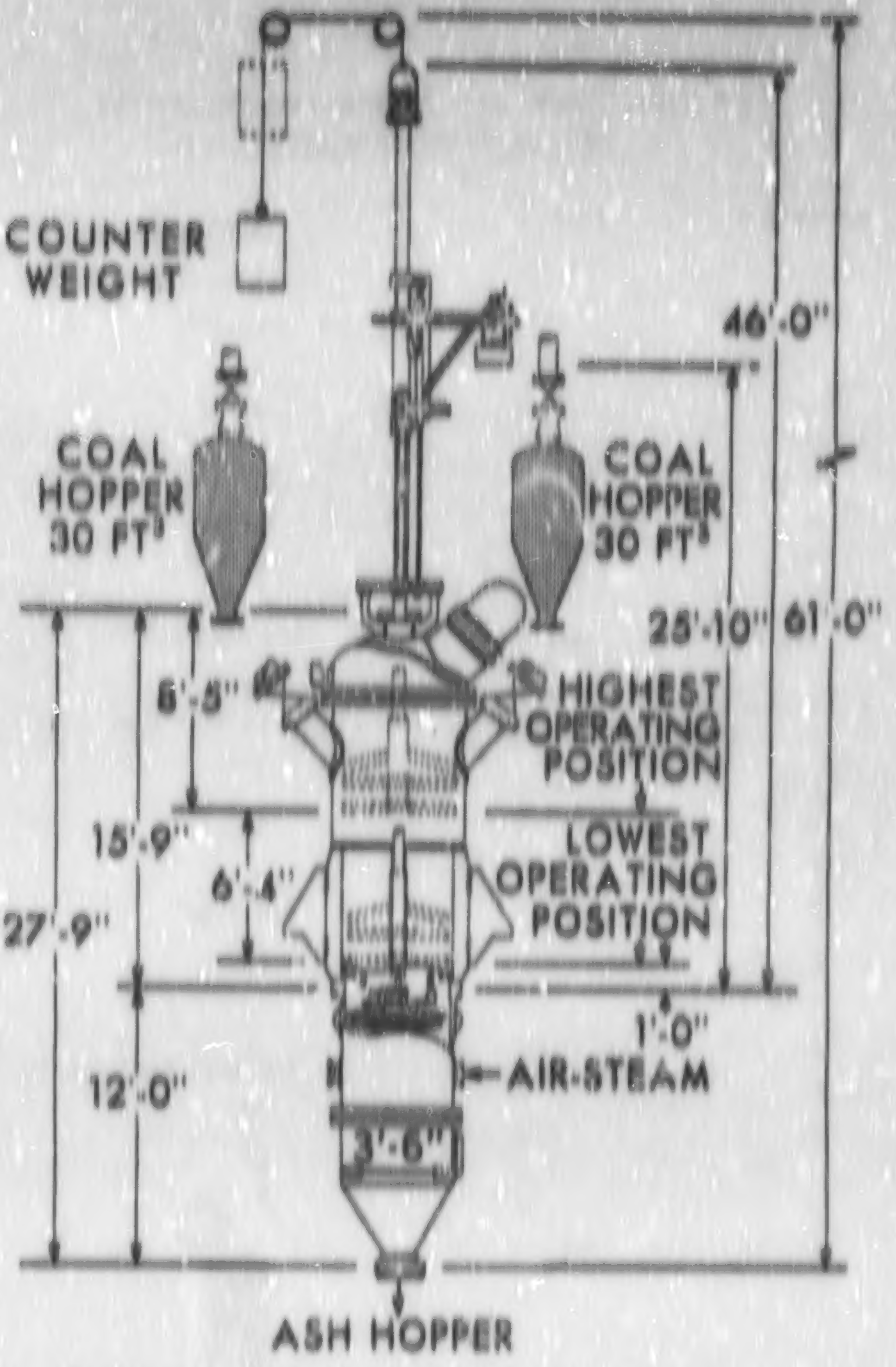

COUNTER WEIGHT
46'-0"
COAL HOPPER 30 FT³
COAL HOPPER 30 FT³
25'-10"
61'-0"
6'-5"
HIGHEST OPERATING POSITION
15'-9"
LOWEST OPERATING POSITION
6'-4"
27'-9"
1'-0"
AIR-STEAM
12'-0"
3'-6"
ASH HOPPER

Figure 4-10. Stirred, pressurized, gas producer.

TABLE A-5. TYPICAL DATA FOR A STIRRED-BED GASIFIER FOR NEW MEXICO SUBBITUMINOUS COAL[16]

RUN-PERIOD	62-2
A. Coal	
FSI	2
H_2O %	8.8
Ash	24.2
C	50.8
H	5.1
S	1.0
N	1.6
O	8.5
Btu/lb	8900
B. Bottom Ash, %, (Dry Basis)	
Ash	94.6
C	4.1
H	.6
S	.2
C. Tar, % (Dry Basis)	
Ash	8.1
C	77.6
H	6.6
S	1.3
N	1.0
Btu/lb	13965

Pressure (psig)	145
Input, lb/hr	
Coal	1200
Air	4583
Steam	783
Input Ratios, lb/lb	
Steam:Coal	.6
Air:Coal	3.8
Output, lb/hr	
Ash	330
Cyclone Dust	86
Gas	5784
Tar	51
Water	889
Gas Yield	
MSCFH	77.7
SCF/lb coal	63.4
Gas Analysis (vol. %)	
CO	15.3
CO_2	12.7
N_2	58.1
H_2	10.7
CH_4	2.1
C_2H_6	0.0
H_2S	.2
O_2	0.0
Heating Value	104 Btu/CF

TABLE 4-7. WATER EQUIVALENT HYDROGEN BALANCE FOR THE STIRRED FIXED BED PROCESS

Actual coal feed: 1,490 lb/hr

	gals/10^6 Btu of product gas
IN	
Moisture in coal	1.6
Water equivalent of hydrogen in coal	7.9
Steam to gasifier	11.5
	21.0
OUT	
Water in product gas	10.9
Water equivalent of hydrogen in gas	10.1
	21.0

Table 4-7 presents the water equivalent hydrogen balance of the relevant process streams for the stirred bed producer gasification process. The numbers are based on the results of the Bureau of Mines research studies converted to units of gal/10^6 Btu of product gas.

4.8 MOLTEN SALT PROCESS

The Kellogg Molten Salt process has been studied in many variations with time.[39-43] Coal is gasified by steam alone in a bath of molten sodium carbonate. The heat absorbed by the gasification reaction cools the salt bath. The molten salt, with carbonaceous char and ash, is circulated from the gasifier to the combustor where air is introduced. Residual carbon burns and reheats the salt. A sidestream of molten salt is continuously treated to remove ash. Figure 4-11 shows a system with the gasifier and combustor in a single, partitioned vessel. Figure 4-12 shows a two-vessel system. Typical temperatures are shown on the figures. Synthesis gas is produced under a pressure of about 400 psi. Pressures up to 1000 psi have been tested. At high pressures oxygen, and not air, would probably be used whether or not pipeline gas is the desired product because of the expense of compressing the nitrogen in the air.

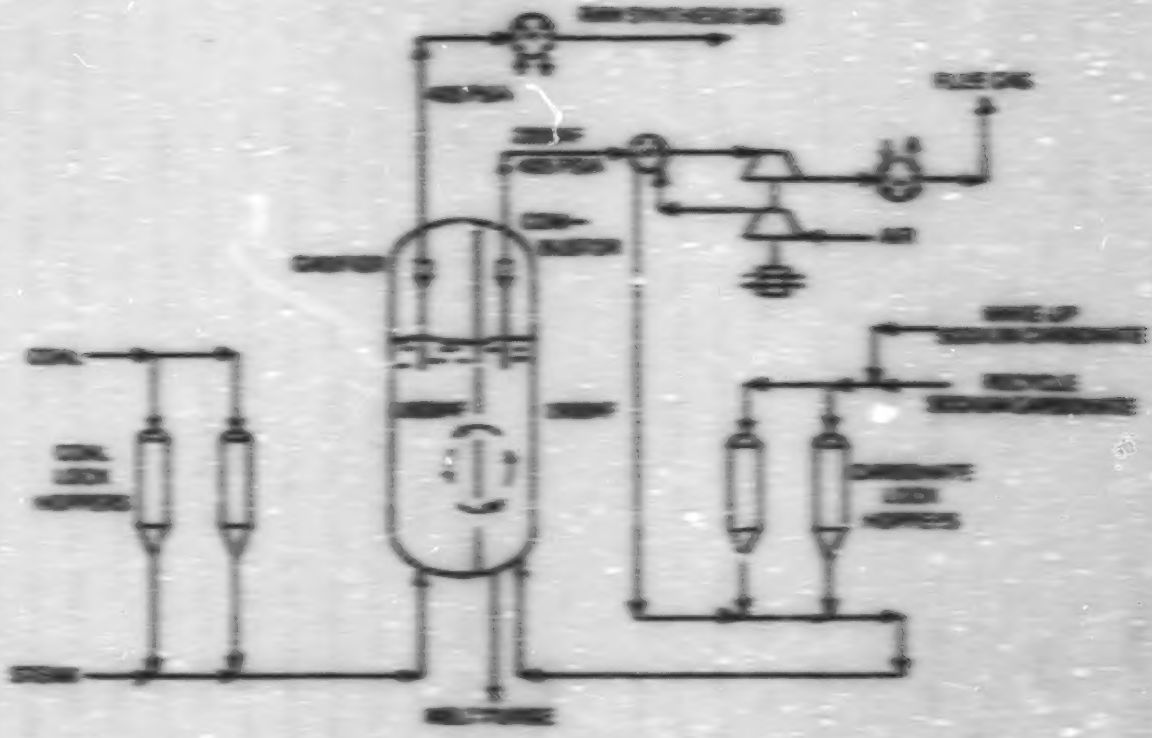

FLUE GAS
AIR
MAKE-UP SODIUM CARBONATE
COAL
STEAM

Figure 4-11. Molten Salt Process gasifier and combustor in a single vessel[42].

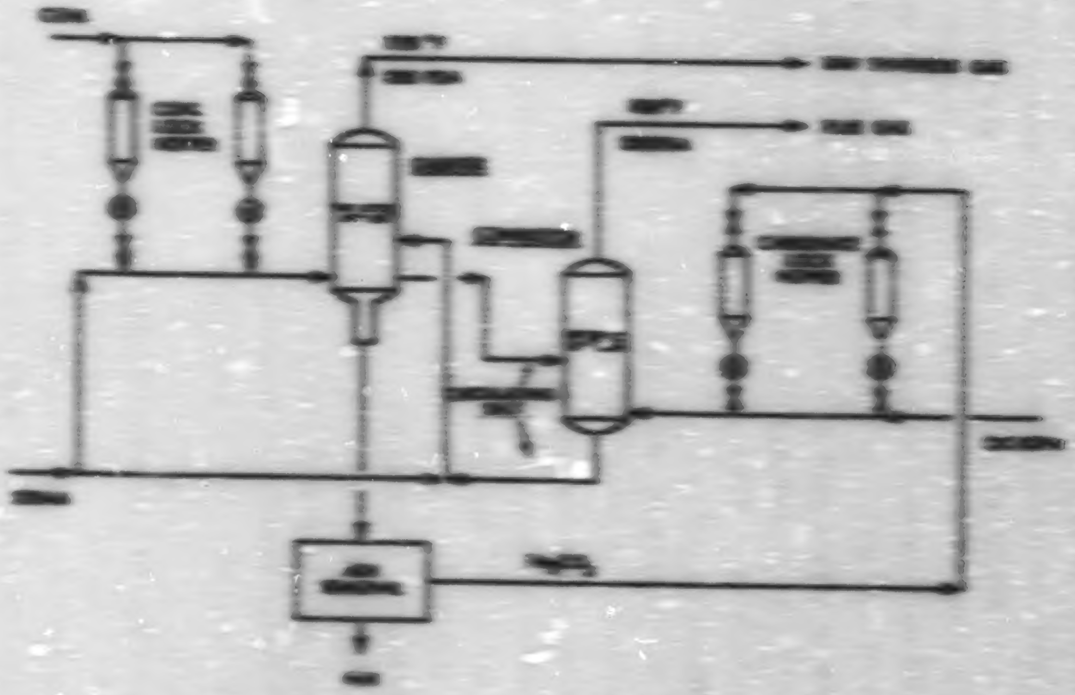


Figure 4-[illegible]. Flow diagram for Molten Salt gasification section using two vessels.

Sulfur in the coal accumulates in the bath as sodium sulfide until the following equilibrium is established:

$$Na_2S + CO_2 + H_2O \rightleftharpoons Na_2CO_3 + H_2S$$

Hydrogen sulfide begins to leave with the gas. Ash accumulates in the molten salt and a purge stream is removed to hold the ash at about 8 percent. The purge stream treatment is shown in Figure 4-11. The stream is quenched to 400°F with a solution saturated with sodium bicarbonate at 100°F in the quench tower. Solid melt particles in the resulting slurry are ground to facilitate dissolution of the salt. This stream is then flashed to essentially atmospheric pressure into a holding tank, where sufficient residence time is provided to dissolve the sodium carbonate. The slurry leaving this vessel is filtered to separate the ash and carbon from the solution. This residue is sent to disposal.

The solution leaving the filter flows to a carbonation tower where the sodium carbonate is reacted with carbon dioxide from the gas purification system. The tower operating temperature is about 100°F. At this temperature the sodium bicarbonate concentration exceeds its solubility limit and is precipitated from solution. The slurry is then filtered; the bicarbonate leaving the filter is calcined to decompose the bicarbonate to carbonate and is returned to the combustor, while the solution is recycled to the quench tower.

Reference 39 is a design of a pipeline gas plant. A hydrogen balance for this plant is presented in Table 4-8. This balance should be treated as being only an indication because it is based on somewhat outdated technology. For this reason it has not been adapted to production of power gas.

4.9 THE LURGI PROCESS FOR UTILITY FUEL GAS PRODUCTION

In this section a very brief mention will be given of recent developments by the British Gas Corp. and Lurgi in running the gasifier in a slagging mode.[44]

Lurgi gasifiers for SNG production are oxygen blown and use about 7 moles steam/mole oxygen with Navajo coal and up to 9 moles steam/mole oxygen with lignite; 45 to 50 percent of the steam is decomposed. Lurgi

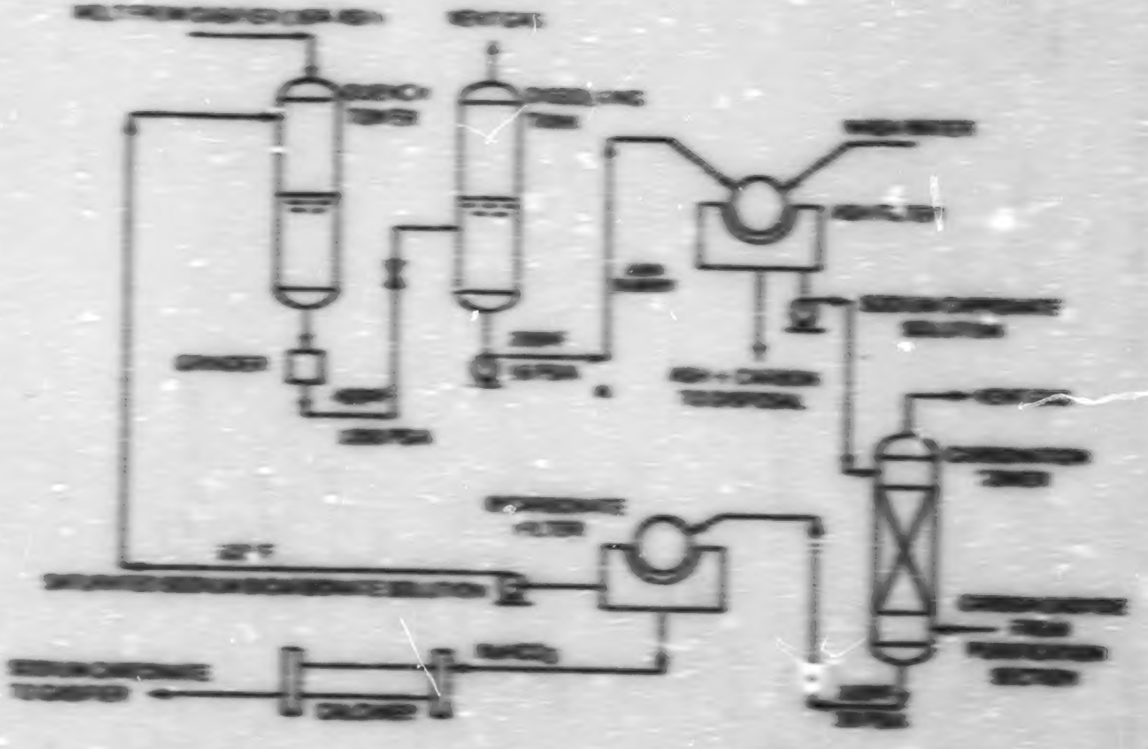


Figure 6-11. Flow diagram of an ash removal system[42,43].

TABLE 4-5. WATER EQUIVALENT HYDROGEN BALANCE FOR THE MOLTEN SALT PROCESS

Coal feed: 1,100,000 lb/hr of run-of-mine bituminous coal (2.0 wt.% moisture and higher heating value of 13,000 Btu/lb).

Product pipeline gas: 250 x 10^6 SCF/day with heating value of 914 Btu/SCF.

	10^3 lb/hr	gals/10^6 Btu product gas
IN		
Moisture in coal	22	0.3
Water equiv. of hydrogen in coal	515	6.5
Steam to gasifier	1,000	12.6
Boiler feed water to shift conversion	147	1.9
Clean water to scrubber	360	4.5
Process water to ash removal	607	7.7
	2,651	33.5
OUT		
Process condensate from shift conversion	163	2.1
Process condensate from scrubber	582	7.3
Condensate from methanation	313	3.9
Water condensate from ash removal	413	5.2
Water in residue from ash removal	3	-
Water equiv. of hydrogen in vent gases from purification and ash removal (CH_4, H_2 and H_2S)	13	0.2
Water vapor to stack from gasification, purification and ash removal	291	3.6
Water equiv. of hydrogen in product gas	908	11.5
	2,687	33.8

gasifiers for utility fuel gas production are air blown and use about 3.77 moles steam/mole oxygen in air (this equals 7.5 moles steam plus nitrogen/mole oxygen) and 45 percent of the steam is decomposed. In the slagging mode the oxygen/carbon ratio is slightly increased, but the ratio of steam/oxygen is reduced to about 1.5 and all of the steam is decomposed. Only the coal moisture appears in the gas. This much reduces the steam need and water treatment plant size. Also, when the gas is cooled to remove tars, etc., very little water condenses out. Condensing water is more than half of the cooling load in the utility gas plants. With little water to condense there is little irreversible loss on cooling, and slagging gasifiers have a higher cold gas efficiency than the usual Lurgi gasifier. The experimental gasifier ran at more than four times the throughput of the normal gasifier.[44] There is no doubt that the slagging gasifier will prove most useful.

4.10 KOPPERS-TOTZEK PROCESS

The Koppers-Totzek is a commercially established high-temperature, entrained-flow gasifier capable of partially oxidizing a wide variety of feed stocks. The gasifiers operate at about 0 psig and oxygen, not air, is used.[46-51] Caking coals can be gasified without pretreatment. The coal receives primary crushing and drying followed by simultaneous drying and pulverization using a ball, rod or roller mill. The degree of drying, varying from 2 to 8 percent, depends on the material to be pulverized. The drying medium, either hot flue gas or product gas combusted with excess air, is circulated through the mill. The pulverized coal, of which about 70 percent will pass through 200 mesh, is conveyed with nitrogen from storage to the gasifer service bin and feed bins. Variable speed coal screw feeders then continuously discharge the coal into a mixing nozzle where a mixture of steam and oxygen entrains the pulverized coal. Moderate temperature and high burner velocity prevent the oxidation of the coal in the nozzle.

The gasifier (Figure 4-14) is a refractory-lined steel shell equipped with a steam jacket for producing low pressure process steam. A two-headed burner has heads 180° apart and can handle about 400 tons of coal per day. A four-headed gasifier, with burners 90° apart, can handle about 850 tons of coal per day. The burner heads are spaced so that particles escaping from

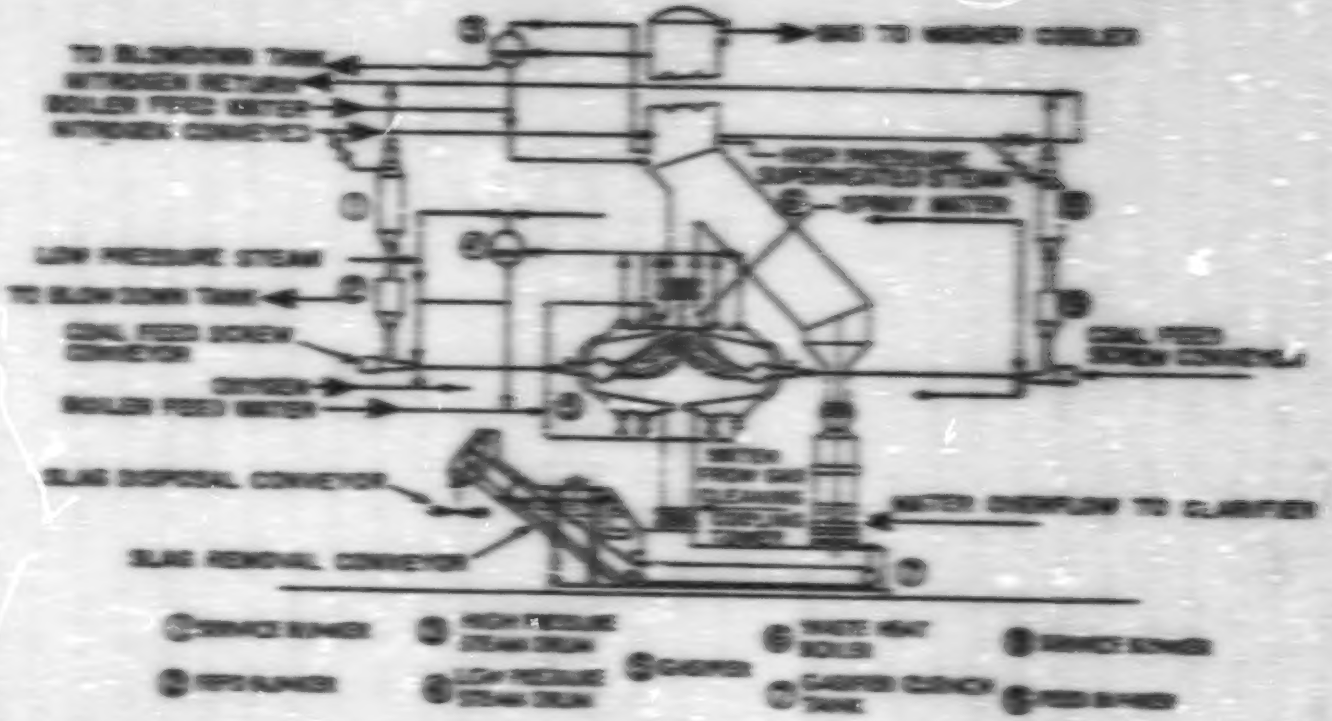

GAS TO WASHER COOLER
TO BLOWDOWN TANK
NITROGEN RETURN
BOILER FEED WATER
NITROGEN CONVEYOR
HIGH PRESSURE SUPERHEATED STEAM
SPRAY WATER
LOW PRESSURE STEAM
TO BLOW DOWN TANK
COAL FEED SCREW CONVEYOR
COAL FEED SCREW CONVEYOR
OXYGEN
BOILER FEED WATER
WATER FROM GAS CLEANING COOLING TOWER
WATER OVERFLOW TO CLARIFIER
SLAG DISPOSAL CONVEYOR
SLAG REMOVAL CONVEYOR
SERVICE BLOWER
HIGH PRESSURE STEAM DRUM
LOW PRESSURE STEAM DRUM
GASIFIER
WASTE HEAT BOILER
GASIFIER QUENCH TANK
SERVICE BLOWER
FEED BLOWER

Figure 4-24. Koppers-Totzek gasifier and heat recovery system.

one burner will be burnt in the opposite burner. Gasifiers currently under design will operate at about 5 psig so that the exiting gases have enough pressure to pass through venturi scrubbers. Carbon is oxidized in the gasifier producing a high temperature flame zone of about 3300-3500°F. The endothermic carbon-steam reactions reduce the exit temperature to around 2700°F. The coal is gasified almost completely and instantaneously. Carbon conversion depends on the reactivity of coal and is about 90-98 percent. At the prevailing high operating temperatures, gaseous and vaporous hydrocarbons emanating from the coal decompose so rapidly that coagulation of coal particles during the plastic stage does not occur. Thus any coal can be gasified regardless of the caking property, ash content or ash fusion temperature. Also, only gaseous products are produced; no tars, condensable hydrocarbons or phenols are formed. Approximately 50 percent of the coal ash drops out as slag into a slag gasifier as fine fly ash.

Gas leaving the gasifier may be direct-water quenched to solidify entrained slag droplets, if necessary, and then passes through a waste heat boiler where high pressure steam is produced. The gas exiting the waste heat boiler at 350-500°F is then scrubbed and cooled to approximately 95°F. The entrained solids are reduced to 0.002-0.005 grain/SCF. Particle-laden water from the gas scrubbing and cooling system is piped to a clarifier. The recovered clean water is cooled and recirculated through the gas washing system (see Figure 4-15).

The gas contains approximately 95 percent of the total sulfur in the coal, and this is removed by any appropriate process.

Table 4-9 presents a water equivalent hydrogen balance of the relevant process streams for a plant manufacturing 250 × 10^6 SCF/day of medium-Btu power gas (from Reference 47 and personal communication from G.V. McGurl of Koppers Engineering and Construction).

For reasons given in Section 7, the Koppers-Totzek process is used in our Solvent Refined Coal plant to gasify the filter residue. This is a particularly high ash material, and in order to make material balances it was necessary to extrapolate from actual operating experience. A study of References 43, 46, and 49 suggested the following performance with a high ash coal in which the H/C ratio (lb/lb) is more than about 0.77:

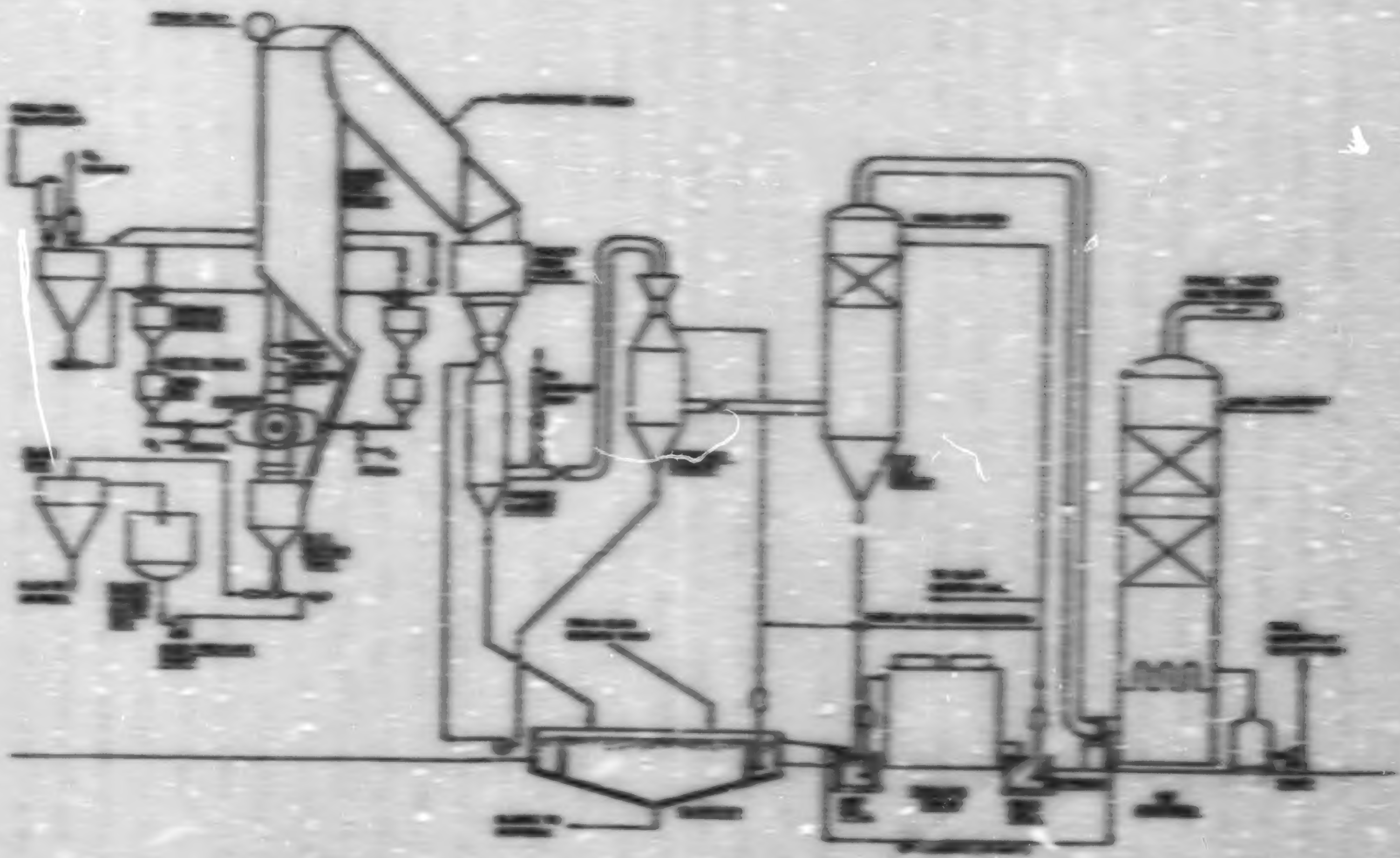


Figure 4-23 [illegible] purification process.

TABLE 4-3. WATER EQUIVALENT HYDROGEN BALANCE FOR THE KOPPERS-TOTZEK PROCESS

Coal feed: 480,605 lb/hr of as-received bituminous coal (16.5 wt.% moisture and 4.77 wt.% hydrogen, higher heating value of 8810 Btu/lb).

Product power gas: 190 x 10^6 SCF/day with higher heating value of 303 Btu/SCF (32.6 dry mole % hydrogen and 0.1 dry mole % methane; moisture is estimated as 0.5 mole %).

	gal/10^6 Btu product gas
IN	
Moisture in coal	3.0
Water equiv. of hydrogen in coal	6.2
Steam to gasifier	2.7
Water to gasifier for spraying hot gas	1.6
Water to purification for makeup	0.1
	13.6
OUT	
Water with wet slag from gasifier	0.2
Water with wet ash from scrubbing and cooling	9.0
Condensate from compression	1.1
Condensate in cooling (net)	0.8
Water vapor in vent gas from coal drier	2.1
Water vapor from purification to Claus	0.0
Water equiv. of hydrogen from purification (H_2S)	0.1
Water equiv. of hydrogen in product gas	0.1
Water vapor in product gas	0.2
	13.6

oxygen feed, lb/lb (carbon + hydrogen) 1.08

steam feed, lb/lb (carbon + hydrogen) 0.183

Mole fractions of gases leaving the reactor to be such that

$$\frac{(H_2)(CO_2)}{(CO)(H_2)} = \text{(approx.) } 0.5$$

Note that methane is not produced in this gasifier.

4.11 H-COAL PROCESS

Hydrocarbon Research, Inc. (HRI) has developed a process for coal liquefaction by catalytic hydrogenation in an ebullated-bed reactor. HRI has conducted bench-scale experiments since 1965, using reactors about 3/4 inch ID and handling about 25 lb of coal per day. Development work was continued on Process Development Units (PDU) using reactors about 8.5 inch ID and handling about 3.5 tons/day of coal feed, representing a scale-up factor of about 300. HRI is now building a prototype demonstration plant. It will have a hydrogenation reactor of 4.5 ft ID capable of processing 250 to 750 tons/day of coal depending on whether synthetic crude or low-sulfur fuel oil is the desired product (725 bbl/day of synthetic crude or 2250 bbl/day of fuel will be produced). This represents a scale-up factor of 100 from the PDU. The commercial size reactors would represent a scale-up factor of 10 from the prototype unit. More description on the Process Development Units and experimental data can be found in References 52-55.

Process designs and economic evaluations have been made[54] for converting an Illinois coal to gasoline and furnace oil, and to gasoline, LPG and benzene. Ammonia and sulfur are produced as byproducts in all cases. As an example we consider the liquefaction of an Illinois coal to gasoline and furnace oil. The capacity of the refinery has been scaled to 50,000 bbl/day of liquid products.

As-received coal is dried, pulverized and slurried with coal-derived oil for charging to the coal hydrogenation unit shown in Figure 4-16. The reactor operates at 3000 psi and contains an ebullated bed of cobalt-molybdenum catalyst wherein the coal is catalytically hydrogenated and converted to liquid and gaseous products. In the ebullated bed the upward passage of the solid, liquid and gases maintains the catalyst in a fluidized state. Catalyst can be added and withdrawn continuously to keep a constant level of activity. Reactor temperature is controlled by the preheat temperature of the hydrogen feed stream. The hot gas is subjected to partial condensation and further phase separation, after which the remaining gas is passed through an absorber for removal of as much hydrocarbon as possible and sent to the hydrogen plant. The synthetic crude produced can be refined to gasoline and furnace oil. The detail of the refining process is described in References 54 and 55 and is not included in this report.

About 90 wt percent of the oxygen in the coal is converted to water which is sent to a sulfur and ammonia recovery section. Much of the remaining oxygen leaves the hydrogenation step as phenols and other oxygenated aromatics.

Hydrogen consumption is approximately 40,000 SCF per ton of coal charged. This is for the production of gasoline and fuel oil. For the production of fuel oil alone the hydrogen consumption can be halved. Table 4-10 presents a water equivalent hydrogen balance supplied by Hydrocarbon Research, Inc. (communication from F.D. Hoffert). This balance matches the simplified flow diagram shown on Figure 4-17.

Hydrocarbon Research, Inc. has also considered the production of a low-sulfur residual fuel oil from a West Virginia,Pittsburgh seam coal. The flow diagram is shown in Figure 4-18. In this case the vacuum bottoms slurry containing coal residue is used to produce the hydrogen required for hydrogenation by partial oxidation which is similar to our design of a Solvent Refined Coal plant. The water equivalent hydrogen balance for this case is shown in Table 4-11.

4.12 SYNTHOIL PROCESS

This process for the hydrogenation of coal to low-sulfur liquid fuel oil is undergoing laboratory development at the U.S. Energy Research and

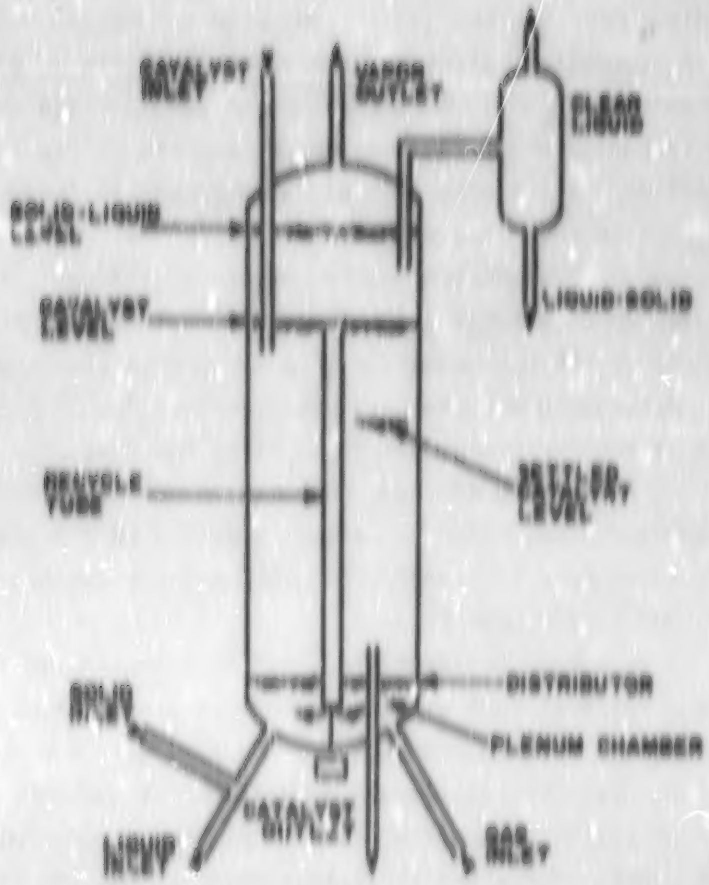

CATALYST INLET
VAPOR OUTLET
SOLID-LIQUID LEVEL
CATALYST LEVEL
LIQUID-SOLID
RECYCLE TUBE
SETTLED CATALYST LEVEL
DISTRIBUTOR
PLENUM CHAMBER
CATALYST OUTLET
LIQUID INLET
GAS INLET

Figure 4-16. H-Coal ebullated-bed reactor.

TABLE 4-10. WATER EQUIVALENT HYDROGEN BALANCE FOR THE H-COAL PROCESS - 1

Coal feed: 1,196,865 lb/hr dry Illinois Coal (4.8 wt. % hydrogen and 9.2 wt. % oxygen as fed to the hydrogenator).

Product oils: Nominal 50,000 bbl/day of product oils (33,051 bbl/day of gasoline, 16,667 bbl/day of domestic fuel oil and 1,113 bbl/day of No. 6 fuel oil).

	10^3 lb/hr	gals/10^6 product oil
IN		
Water equivalent of hydrogen in dry coal	517	4.9
Steam to hydrogen plant	408	3.9
	925	8.8
OUT		
Waste water from sulfur and NH_3 recovery	133	1.3
Water equivalent of hydrogen in byproduct NH_3	21	0.2
Water equivalent of hydrogen in coal residue	79	0.7
Water equivalent of hydrogen in self-generated fuel gas	39	0.4
Water equivalent of hydrogen in product oil mix[a]	653	6.2
	925	8.8

---

[a] Determined by difference equivalent to 12.2 wt. % hydrogen in the oil mix, HHV approximated as 140,000 Btu/gal.

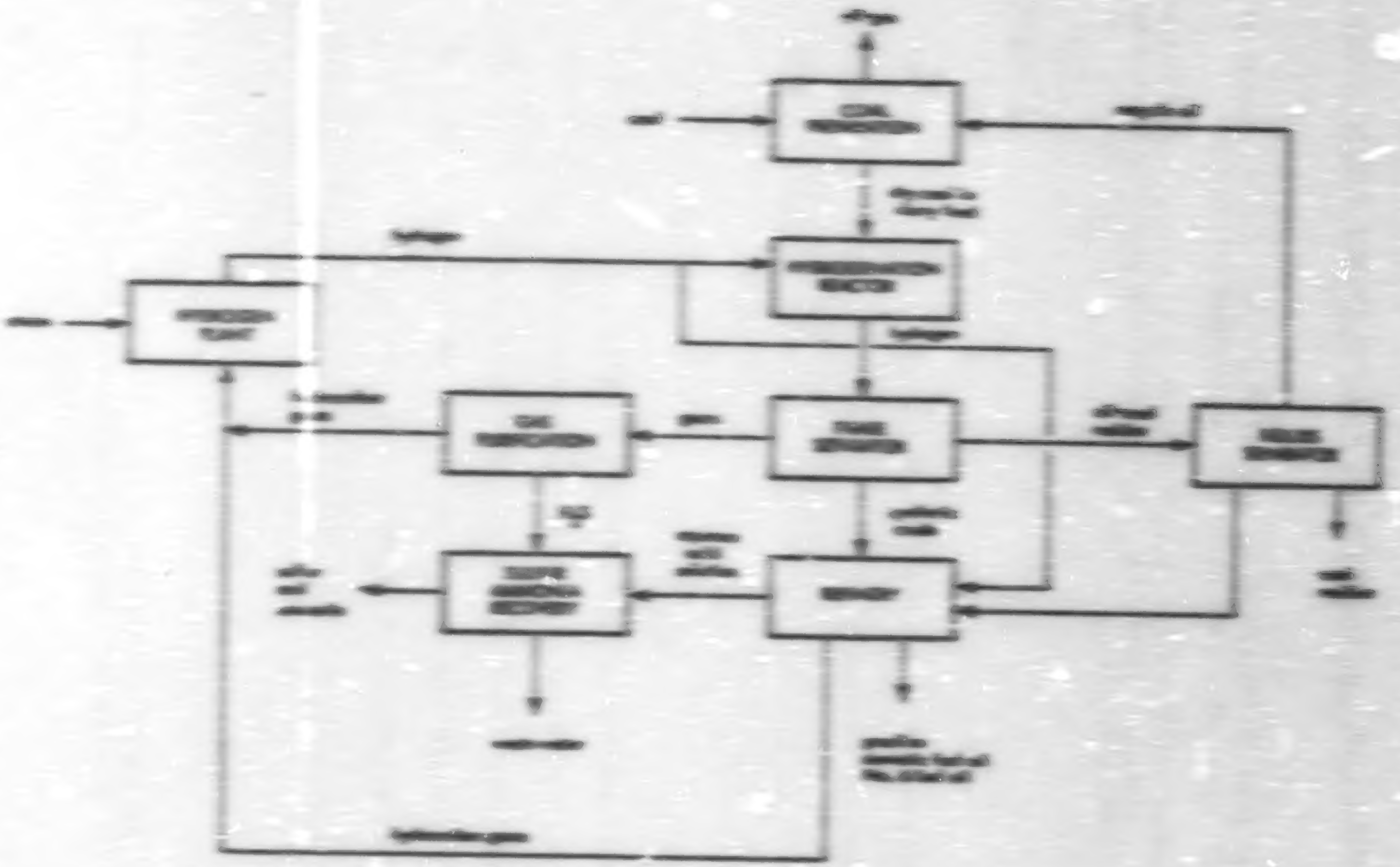


Figure 4-27. Flow diagram for process water streams in H-Coal process for production of 50,000 bbl/day of product oils.

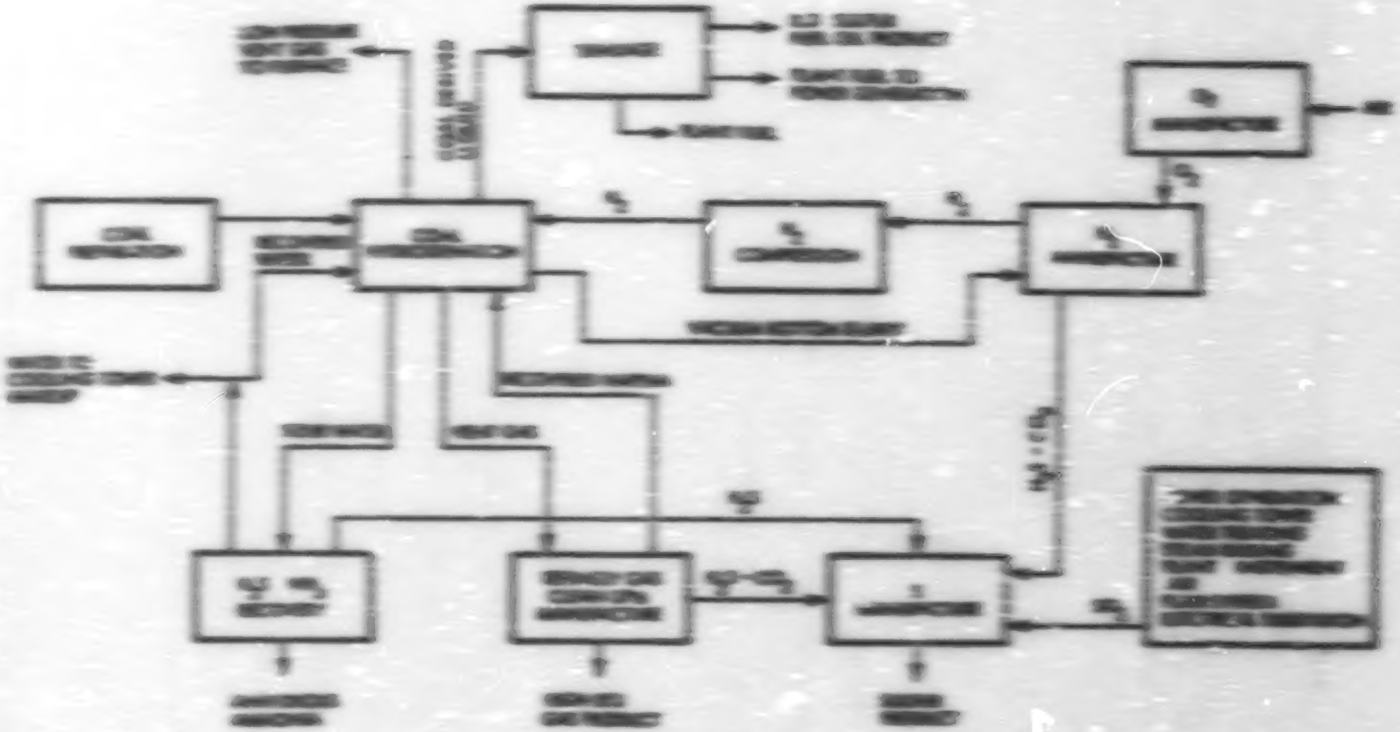


Figure 4-[illegible]. Block flow diagram for [illegible] process.

TABLE 4-11. WATER EQUIVALENT HYDROGEN BALANCE FOR THE H-COAL PROCESS - 2

Coal feed: 1,494,208 lb/hr as-received Pittsburgh seam coal
(5.7 wt. % hydrogen).
Products: 61,041 bbl/day fuel oil sold (13,595 bbl/day slurry used in production of hydrogen and in plant fuel requirements), and 128.1 x 10^6 SCF/day gas with lower heating value of 870 Btu/SCF.

	10^3 lb/hr	gals/10^6Btu products
IN		
Water equivalent of hydrogen in feed coal	767	5.6
Water consumed in hydrogen manufacture	459	3.4
	1226	9.0
OUT		
Waste water from S and NH_3 recovery	134	1.0
Water equivalent of H_2 in product gases	477	3.5
Water equivalent of H_2 in refinery gases used as fuel	0.6	0.0
Water equivalent of H_2 in waste gases to flare	0.6	0.0
Water equivalent of H_2 in byproduct NH_3	37	0.3
Water equivalent of H_2 in slurry used to produce power and used as plant fuel	102	0.7
Water equivalent of H_2 in product oils[a]	513	3.8
	1264	9.3

---

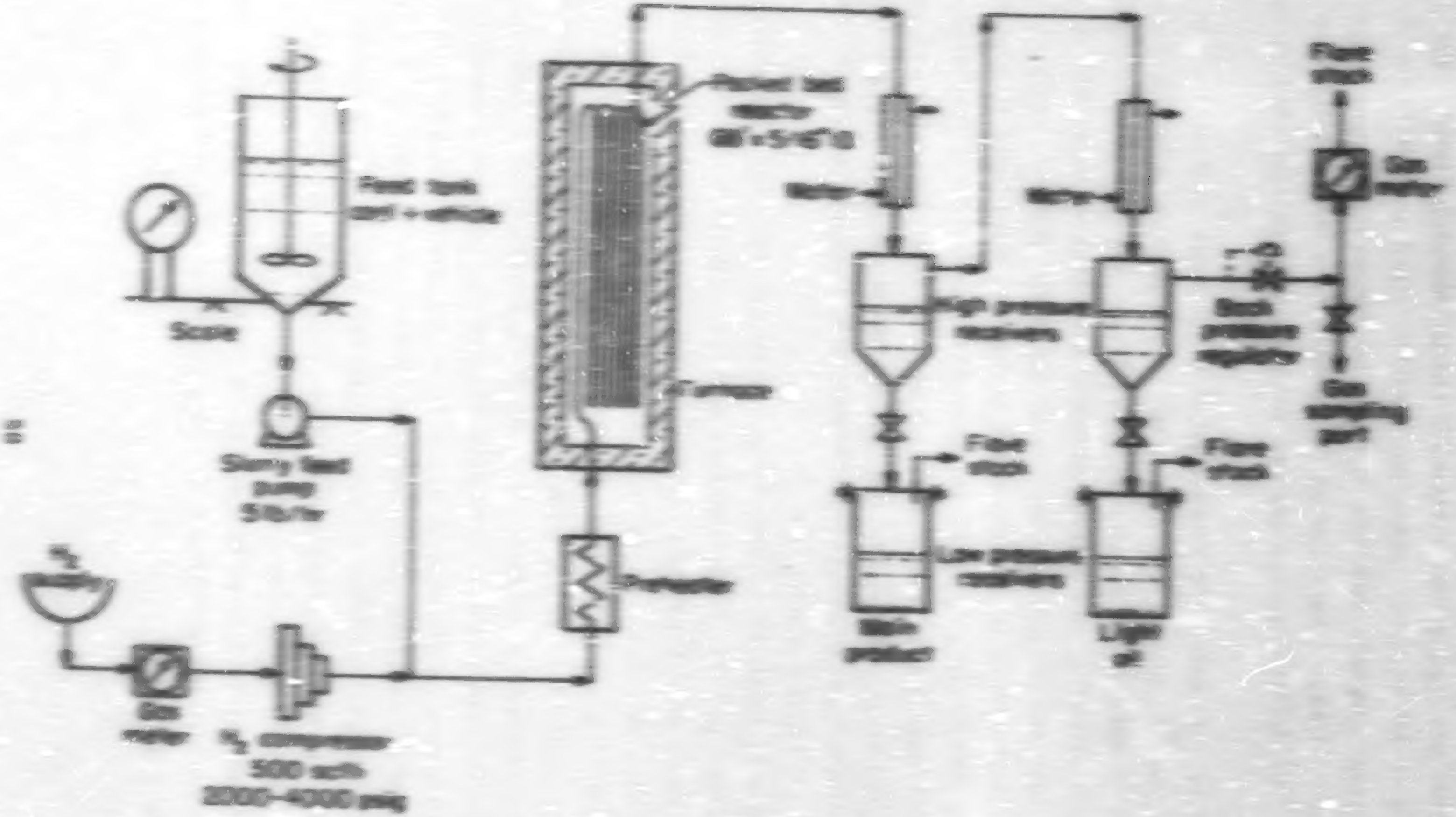
[a] 10.4 wt. % H_2 in the oil, HHV approximated as 157,400 Btu/gal.

Development Administration, Pittsburgh Energy Research Center. Early work using a 5 lb (slurry)/hr reactor has been described in References 56-58. The process gives a mobile fuel oil (7.6 percent hydrogen or more, molar ratio of C/H about 1/1) with a very low sulfur content from coals having 4 to 5 percent sulfur. The desulfurization aspects are particularly discussed in References 58-60.

Figure 4-19 shows the present pilot plant which handles 1/2 ton (slurry)/day.[61] Coal of 200 mesh dried to 0.5 percent moisture content is slurried to about 35 wt percent in recycle oil, mixed with hydrogen, preheated and passed up one or two reactors, each 14.5 ft long and 1.1 inch ID. The reactors are packed with pellets of cobalt-molybdenum catalyst. Flow through the reactors is two-phase and turbulent; the liquid is propelled by the gas. The reactor operates at about 450°C and 2000 psi or more.

Upon leaving the reactor gas is separated from the liquid and recycled. A steady purge is removed from the gas stream and makeup hydrogen is continuously added. The liquid is centrifuged from suspended solids and some of it is recycled to slurry more coal.

The only integrated plant design (including hydrogen production) which we have seen is that of Reference 63 made for a Wyoming coal and made specifically for cost estimating purposes. For the purpose of estimating water requirements we have, in a separate study (subcontract No. 1916-3 to University of Oklahoma, primary contract EPA 68-01-1410), chosen to make our own, somewhat simplified design. The block diagram of Synthoil liquefaction process is reproduced as Figure 4-20. Based on the experience reported in References 61-63, various rules were made for material balance calculations:
1) five barrels of oil were produced from each ton of carbon in coal;
2) 4700 SCF of hydrogen were needed for one barrel of oil; 3) 6.2 percent of carbon in coal remained in the char to hydrogen plant. About 83 percent of oxygen in coal was converted to water and discharged from phase separator;
4) the hydrogen needed for liquefaction was produced from the gasification of char and as-received coal followed by two water shift reactions. Gasification information was extrapolated from Reference 63 and the production train is shown on Figure 4-21.



Feed tank
Scale
Slurry feed pump
5 lb/hr
H_2 supply
Gas meter
H_2 compressor
500 scfh
2000–4000 psig
Preheater
Furnace
Packed bed reactor
Water
High pressure receivers
Low pressure receivers
Flare stack
Main product
Light oil
Gas meter
Back pressure regulator
Gas sampling port

Figure 4-[illegible]. Synthoil pilot plant.

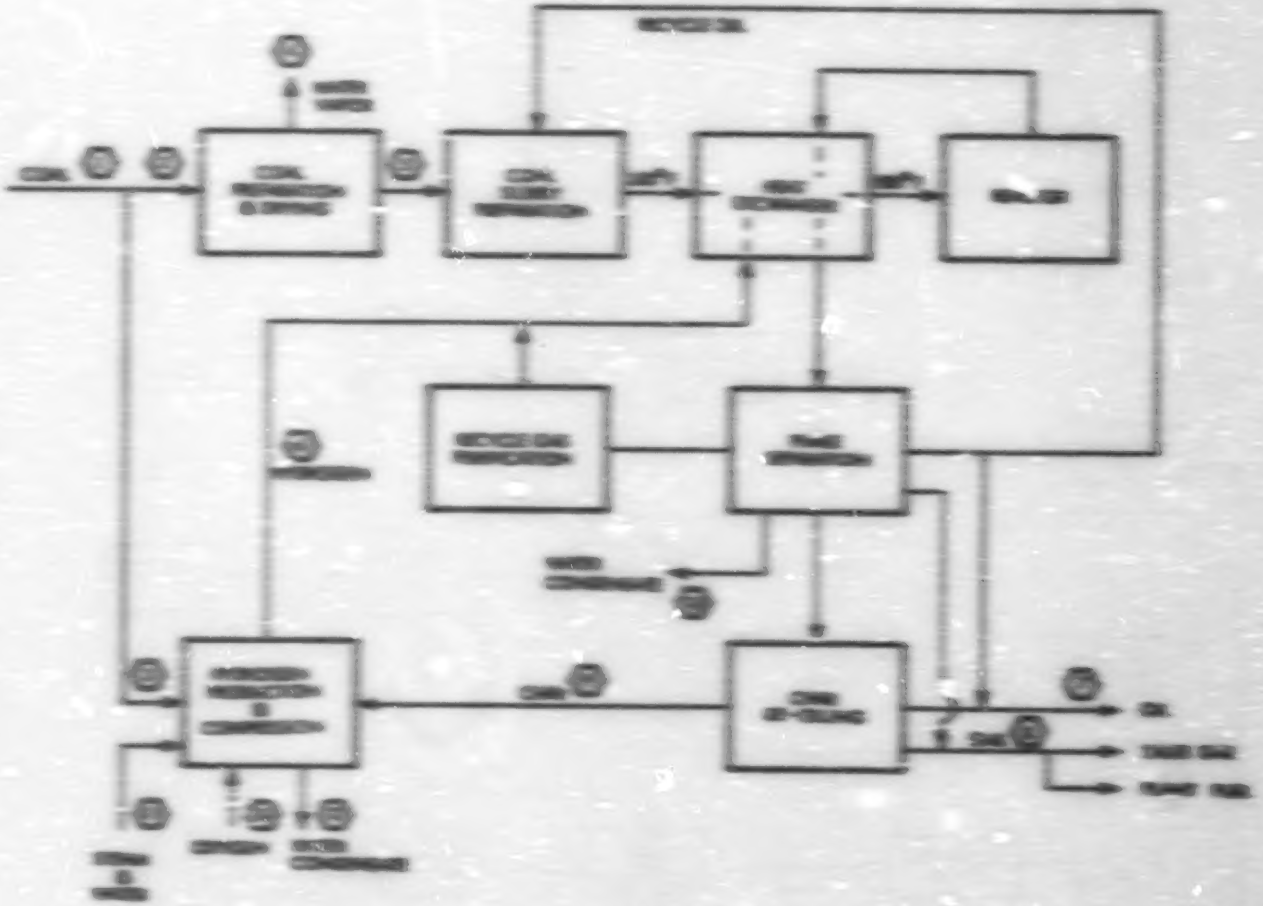


Figure 4-21. Flow diagram for process water streams in Synthoil process.

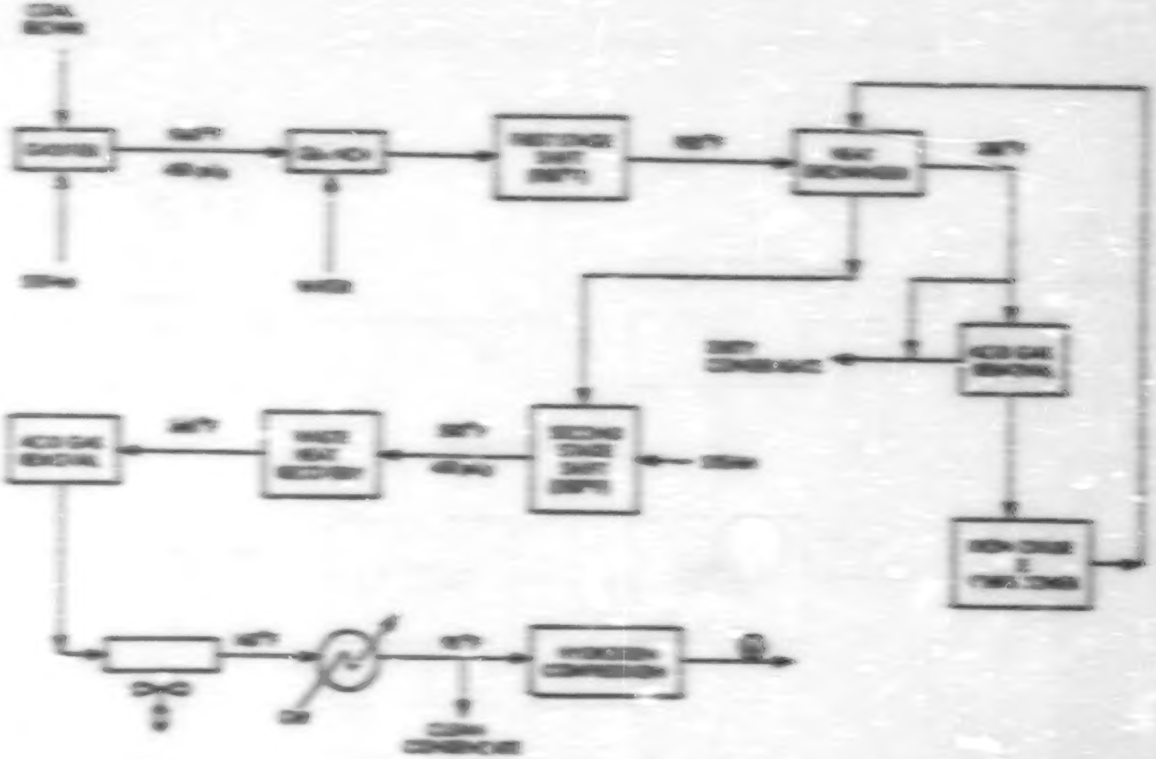


Figure 4-21. Flow diagram for hydrogen production in Synthoil process.

TABLE 4-12. APPROXIMATE COAL ANALYSES FOR SYNTHOIL PROCESS

	As-received coal composition (%)		
	New Mexico Subbituminous	Wyoming Subbituminous	North Dakota Lignite
C	47.3	49.4	40.8
H	3.4	3.4	2.7
N	0.8	0.5	0.5
O	9.6	12.8	11.9
S	0.9	0.3	0.7
Ash	25.6	5.6	7.4
Moisture	12.4	28.0	36.0
HHV (Btu/lb)	8310	8440	6823

Table 4-12 shows the approximate coal analyses at three western sites as used in the separate study mentioned above. These compositions differ somewhat from coals to be used later in other conversion processes in this report. Water equivalent hydrogen balances of a Synthoil plant producing 50,000 bbl/day of oil using these three types of coal are shown on Table 4-13.

TABLE 4-11. WATER EQUIVALENT HYDROGEN BALANCE FOR THE SYNTHOIL PROCESS

Basis: 50,000 barrels/day oil (about 11.45 × 10^9 Btu/hr).
Units: 10^3 lb/hr.

	New Mexico	Wyoming	North Dakota
PROCESS INFORMATION			
As-received coal fed to liquefaction ②	1766	[illegible]	2665
As-received coal fed to gasification ③	334	318	534
HYDROGEN BALANCE			
IN			
Moisture in coal to liquefaction ②	439	947	[illegible]
Water equiv. of hydrogen in coal to liquefaction ②	[illegible]	[illegible]	[illegible]
Moisture in coal to gasification ③	60	178	[illegible]
Water equiv. of hydrogen in coal to gasification ③	207	[illegible]	270
Total steam to hydrogen production ⑬	520	521	467
Quench water to hydrogen production	[illegible]	[illegible]	[illegible]
	[illegible]	[illegible]	[illegible]
OUT			
From drying coal to liquefaction ⑥	[illegible]	[illegible]	[illegible]
Total dirty process condensate ⑫ + ⑬	635	759	[illegible]
Clean process condensate	179	132	96
Moisture in product oil ⑦	[illegible]	[illegible]	[illegible]
Water equiv. of hydrogen in product oil ⑦	26	22	23
Water equiv. of hydrogen and moisture in gas produced ⑧	367	424	484
	[illegible]	[illegible]	[illegible]

(continued)

TABLE 4-11. (Continued)

Units: gals/10^6 Btu product oil

	New Mexico	Wyoming	North Dakota
IN			
Moisture in coal to liquefaction ②	3.9	3.5	13.2
Water equiv. of hydrogen in coal to liquefaction ②	9.1	9.2	9.0
Moisture in coal to gasification ⑤	0.7	1.6	3.5
Water equiv. of hydrogen in coal to gasification ⑤	1.8	1.7	2.4
Total steam to hydrogen production ⑩	4.7	4.6	4.2
Quench water to hydrogen production ⑩	5.2	4.7	6.0
	25.4	25.3	38.3
OUT			
From drying coal to liquefaction ④	3.8	3.3	13.1
Total dirty process condensate ⑫ + ⑬	5.7	6.8	6.9
Clean process condensate ⑫ + ⑬	1.2	1.2	0.9
Moisture in product oil ⑦	10.2	10.2	10.2
Water equiv. of hydrogen in product oil ⑦	1.1	1.1	1.1
Water equiv. of hydrogen and moisture in gas produced ⑧	3.4	2.7	6.1
	25.4	25.3	38.3

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SECTION 5

HYGAS PROCESS

5.1 INTRODUCTION AND SUMMARY OF RESULTS AT WYOMING SITE

The Hygas process has been under development by the Institute of Gas Technology since 1946. The development of the Hygas process has advanced to the large pilot plant stage with a facility capable of producing 1.5 × 10^6 SCF/day of pipeline gas from 75 tons/day of coal. This pilot plant is now being operated in Chicago, Illinois.

Three different versions of the basic Hygas process, namely, Hygas-Oxygen, Hygas-Steam/Iron and Hygas-Electrothermal, have been designed. Basically these three processes share the same coal pretreatment, material handling, hydrogasification, purification, and methanation systems, but they differ in the technique used to produce the hydrogen-rich stream for hydrogasification.[1-13] In this section the Hygas-Oxygen process is described.

The run-of-mine coal is crushed to -8 × 100 mesh in cage mills and dried to 2 percent moisture content. The coal is then slurried to 50 percent solid concentration (by weight) with recycle slurry oil from downstream in the process. The coal-oil slurry is then pumped to the gasifier operating pressure of 1200 psig and heated in an external heater to 300°F.

The pilot-plant hydrogasifier is 135 ft high, 5.5 ft ID reactor vessel with five internally connected reaction stages (Figure 5-1). The slurry is pumped into the fluidized top section as a spray. Sensible heat in the gaseous products efficiently vaporizes the light oil and leaves dry coal to be fed to the second section.

In the dilute-phase second section, which is the first stage of

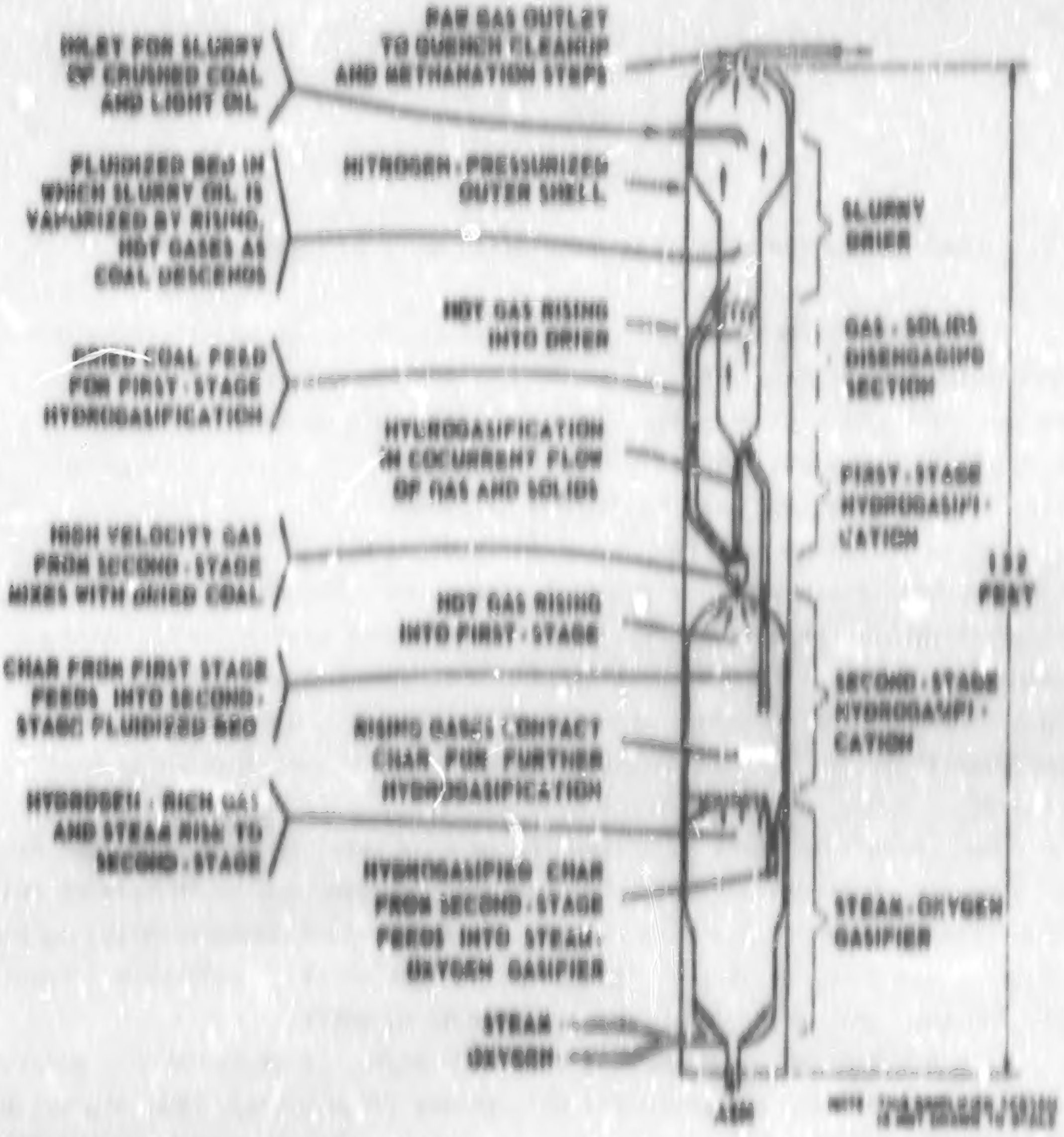
INLET FOR SLURRY OF CRUSHED COAL AND LIGHT OIL
RAW GAS OUTLET TO QUENCH CLEANUP AND METHANATION STEPS
FLUIDIZED BED IN WHICH SLURRY OIL IS VAPORIZED BY RISING, HOT GASES AS COAL DESCENDS
NITROGEN-PRESSURIZED OUTER SHELL
SLURRY DRIER
HOT GAS RISING INTO DRIER
DRIED COAL FEED FOR FIRST-STAGE HYDROGASIFICATION
GAS-SOLIDS DISENGAGING SECTION
HYDROGASIFICATION IN COCURRENT FLOW OF GAS AND SOLIDS
FIRST-STAGE HYDROGASIFICATION
HIGH VELOCITY GAS FROM SECOND-STAGE MIXES WITH DRIED COAL
132 FEET
HOT GAS RISING INTO FIRST-STAGE
CHAR FROM FIRST STAGE FEEDS INTO SECOND-STAGE FLUIDIZED BED
SECOND-STAGE HYDROGASIFICATION
RISING GASES CONTACT CHAR FOR FURTHER HYDROGASIFICATION
HYDROGEN-RICH GAS AND STEAM RISE TO SECOND-STAGE
HYDROGASIFIED CHAR FROM SECOND-STAGE FEEDS INTO STEAM-OXYGEN GASIFIER
STEAM-OXYGEN GASIFIER
STEAM
OXYGEN
ASH

Figure 5-1. IGT Hygas pilot plant hydrogasification reactor[9].

hydrogasification, hot gases at about 1700°F rising from the second stage of hydrogasification react with the coal in concurrent flow. About 20 percent of the coal is converted to methane in this stage which is operated at about 1300°F. In the second stage of hydrogasification, hydrogen reacts exothermically with the char to produce methane while steam reacts endothermically with char to produce CO and more hydrogen. An additional 25 percent of the coal is converted in this stage. The hot char descends to the final dense phase fluidized bed where the hydrogen-rich gas is produced in the presence of steam and oxygen.

The Hygas-Oxygen process has been chosen for a detailed study at the Wyoming, New Mexico and North Dakota sites. The detailed design is presented only for the Wyoming site. The gasifier details using Wyoming subbituminous coal have been supplied by IGT and the rest of the plant has been calculated so as to minimize water consumption. The water equivalent hydrogen balance at the Wyoming site, giving all process water streams, is shown on Table 5-1. Table 5-2 shows the ultimate disposition of unrecovered heat from which the cooling water requirements will be calculated in Section 10. The analysis of the Wyoming subbituminous coal used is shown on Table 5-3.

5.2 MATERIAL BALANCE, WYOMING

The gas production train is shown on Figure 5-2. Stream compositions are shown on Table 5-4 and the ash residue composition is shown on Table 5-5. The streams into and out of the gasifier were supplied by IGT. This gasifier information represents IGT's best, conservative estimate of the performance of the Hygas reactor system using Wyoming coal. All other streams have been calculated.

The raw off-gas contains materials other than fuel gas species. For example, the oil made in this type of gasifier is expected to be approximately 85 percent toluene and 15 percent benzene with a small quantity of phenol. The oil manufactured in the Hygas reactor is significantly lighter than most other gasification systems. The oil made about equals the oil lost in purification or left in the product gas. No oil is sold.

Most of the nitrogen in the coal is converted to ammonia. The remainder

TABLE 5-1. WATER EQUIVALENT HYDROGEN BALANCE FOR HYGAS PROCESS USING WYOMING SUBBITUMINOUS COAL

Coal feed: 1,314,500 lb/hr as-received subbituminous coal (19.9% moisture, 4.03% hydrogen), dried to 2% moisture as fed to gasifier.

Product gas: 250 x 10^6 SCF/day product gas (95.44 vol % methane, 1.72 vol % hydrogen) with a HHV of 968.6 Btu/SCF.

	10^3 lb/hr
IN	
Moisture in as-received coal	261
Water equivalent of hydrogen in as-received coal	477
Steam to gasifier	1015
	1753
OUT	
Moisture from coal drying	240
Condensate in waste heat recovery phase separator	194
Water equivalent of hydrogen from acid gas removal	80
Condensate from methanator	281
Water equivalent of hydrogen in product gas	951
	1746

TABLE 5-1. ULTIMATE DISPOSITION OF UNRECOVERED HEAT IN HYGAS PLANT USING WYOMING COAL

Basis: 250 x 10^6 SCF/day (10.09 x 10^9 Btu/hr)

	10^9 Btu/hr	10^9 Btu/hr
Coal drying	0.26	
Heat in hot condensate water	0.01	
Electricity used + slurry pump dissipation	0.10	
Boiler stack loss	0.20	
Combustibles lost in purification	0.80	
Subtotal - Direct Loss		1.37
Air cooling of plant process stream[a]		0.55
Wet cooling of plant process stream[a]		0.23
Hot ash from gasifier		0.32
Bottom ash quench from boiler		0.002
Total steam turbine condensers		0.65
Total compressor interstage cooling		0.16
Acid gas removal regenerator condenser		0.80
		4.08

---

[a] The heat assumed for water treatment and other uses (Table 5-7) is assumed distributed 50% to dry cooling and 50% to wet cooling.

TABLE 5-3. COAL AND ASH RESIDUE FOR PYGAS PLANT AT WYOMING SITE

Wyodak coal, wt. %

Stream No. in Fig. 5-2	①	③	⑦
	As-Received	Fed to Gasifier	Ash Residue
C	54.2	66.32	17.80
H	4.0	4.93	0.19
N	0.8	0.93	2.01
S	0.6	0.74	0.38
O	14.5	17.74	-
Ash	6.0	7.34	79.62
Moisture	19.9	2.00	-
	100	100	100
HHV (calculated)	9264 Btu/lb		2722 Btu/lb

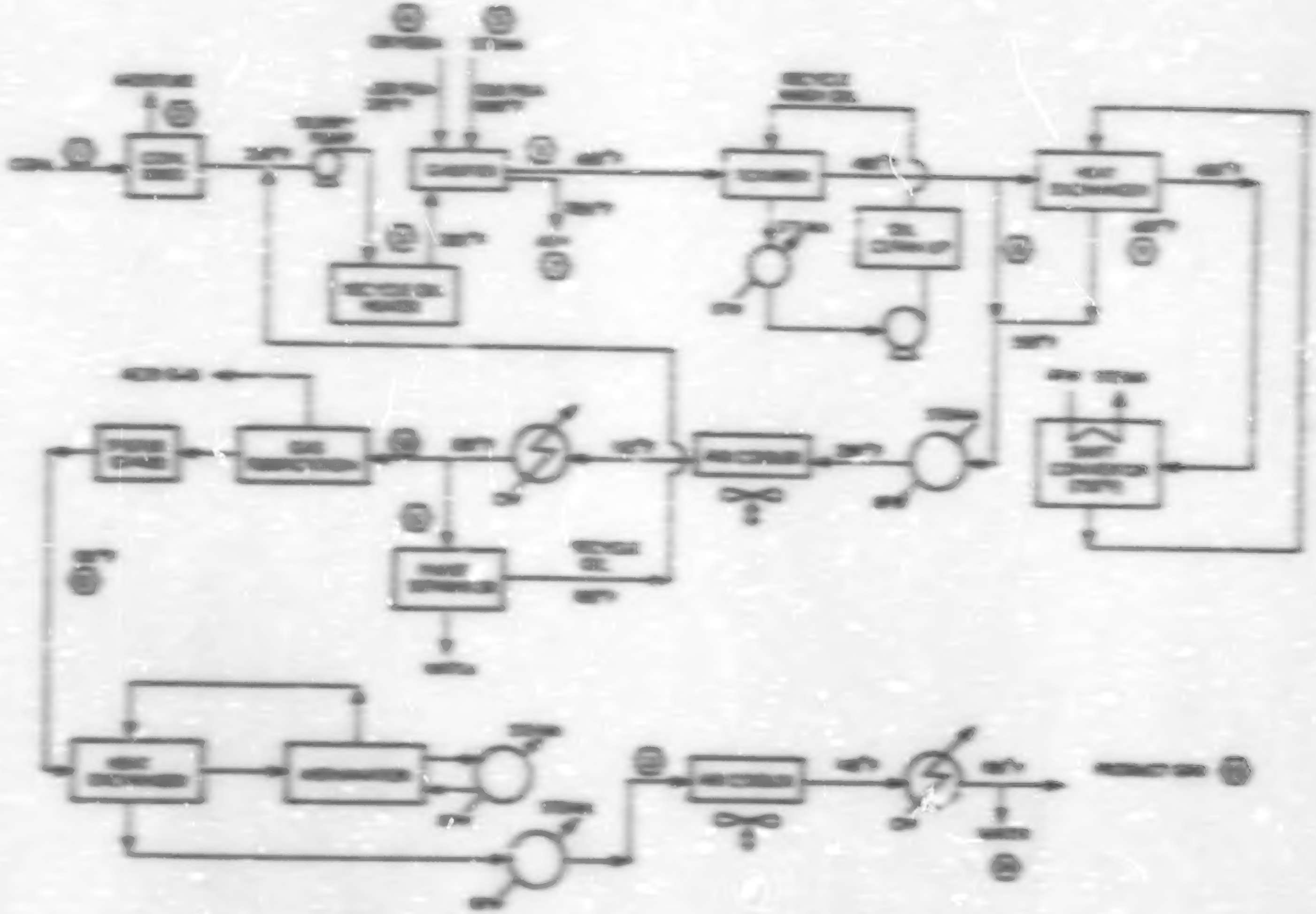

Figure 5-2. Flow diagram for Hygas process.

TABLE 3-6. STREAM COMPOSITIONS FOR COGAS PLANT USING [illegible] COAL (SEE FIGURE 3-[illegible])

Basis: 250 x 10^6 scf/day (10.99 x 10^9 Btu/hr)

STREAMS TO GASIFIER

		10^3 lb/hr
1	As-received coal	1,315
2	Vaporized moisture	180
3	Dried coal in slurry	1,135
4	Slurry oil	1,070
	Composition: C_6H_6: 11 wt. %; C_7H_8: 80 wt. %; C_8/C_9 and C_{10} aromatics: 9 wt. %	
6	Oxygen	669
5	Steam	1,019
7	Ash residue	99,100

PRODUCT STREAMS (10^3 moles/hr)

	6	8	9	10	11	12	13	14	15
CO	20.55	5.36	5.70	31.15		11.10	0.03		0.01
CO_2	10.32	5.02	23.70	38.73		9.01	0.00		9.00
H_2	25.31	6.55	29.05	37.60		26.60	1.08		5.60
CH_4	13.77	3.57	10.19	13.77		13.03	20.10		20.10
C_2H_6	1.06	0.27	0.77	1.0[illegible]		0.70			
Others	0.16*	0.00	0.56	0.76		0.06**	0.06		0.00
H_2O	28.01	6.77	0.70	1.08	16.33		11.00	17.16	0.03
C_6H_6	1.03	0.00	1.13	0.21	1.27				
C_7H_8	10.74	2.76	7.01	0.05	10.01				

* Includes the following components: 60% NH_3, 5% N_2, 8% [illegible], 26% H_2S and 1% COS.

** Mostly nitrogen.

appears as cyanide or free nitrogen gas. However, pilot plant experience indicates that thiocyanate is found in effluent water streams to the exclusion of cyanide even though thermodynamics dictates against formation of thiocyanate in reducing atmospheres. Also, the appearance of free nitrogen is not verified by pilot plant experience since all line purging is done with nitrogen.

Sulfur in the coal is primarily reduced to H_2S. The quantity of COS reported in the off-gas was based upon thermodynamic expectations within the reactor; these same considerations indicate that CS_2 will not be formed, nor will mercaptans or thiophenes. With lignite coal containing one percent sulfur as feedstock, pilot plant data verify the absence of CS_2 and thiophenes; however, trace quantities of methyl mercaptan have been detected.

As in most Hygas process flow sheets, the gasifier product gas is quenched with oil to about 400°F to cool the gas and remove particulate matter. We find that no condensation of water or oil occurs.

A portion of the gas next undergoes shift reaction at an equilibrium temperature of 750°F to adjust the ratio of hydrogen to CO for the downstream methanation reaction. The shifted gas is cooled to 100°F to ensure condensation of the oil. Water also condenses at this point. A circulating water scrub may be used to ensure that all the ammonia, phenol and other soluble species are removed from the gas. It has been assumed that these species can be adequately removed by the quantity of water which condenses. Circulating water has not been shown on Figure 5-2.

A physical-solvent based system, such as the Selexol process, is used for acid-gas removal to recover the remainder of the BTX stream, dehydrate the gas, generate an H_2S-rich gas for sulfur recovery, discharge a CO_2-rich gas with minimum H_2S concentration, and provide a treated gas of sufficient purity that only a nominal sulfur guard is required prior to methanation. Based on the recommendation of IGT, the following losses are assumed to occur in gas purification: 0.5% loss of H_2 and CO, 1% loss of CH_4 and 25% loss of C_2H_6. The process is assumed capable of reducing CO_2 to 1%. All other acid gases were completely absorbed. In view of the relative solubilities of various gases in Selexol solvent,[14] these assumptions are reasonable.

TABLE 5-5. HYGAS GASIFIER HEAT BALANCE USING WYOMING COAL

Basis: 250 × 10^6 SCF/day (10.09 × 10^9 Btu/hr)

	10^9 Btu/hr
IN	
Coal	12.20
Steam (1250 psia, 1000°F)	1.48
Sensible heat of coal slurry	0.11
Sensible heat of oxygen feed	0.02
	13.81
OUT	
Gas	12.54
Hot ash	0.32
Oil made and sensible heat	0.95
	13.81

5.3 HEAT BALANCE, WYOMING

The gasifier information supplied by IGT is in both material and thermal balance. Approximate gasifier heat balance is shown on Table 5-5. The heat balance was then extended to the complete gas production train. The heat exchangers and waste heat recoveries were individually calculated. The balance is shown on Table 5-6. The heating value of ash residue shown is the sum of the higher heating value and sensible heat.

The driving energy required for the plant is shown on Table 5-7. In making Table 5-7 the following rules were used:

(1) To dry coal the water must be evaporated and coal heated to 230°F. The excess sensible heat in coal is contributed to the coal slurry heater in raising the recycle oil to 200°F.

(2) The coal slurry pump operates at 70 percent efficiency and requires 1200 kw.

TABLE 5-6. HYGAS PRODUCTION TRAIN HEAT BALANCE USING WYOMING COAL

Basis: 250 x 10^6 SCF/day (10.09 x 10^9 Btu/hr)

	10^9 Btu/hr
IN	
Coal	12.20
Steam	1.48
Heat for coal drying	.08
Heater for coal slurry	.06
Sensible heat of oxygen	.02
	13.84
OUT	
Product gas	10.09
Steam produced	2.12
Combustibles lost in gas purification	0.80
Sensible heat of condensate	0.01
Dry cooling of process streams	0.41
Wet cooling of process streams	0.09
Hot ash	0.32
	13.84

TABLE 5-7. HYGAS PLANT USING WYOMING COAL: DRIVING ENERGY

Basis: 250 x 10^6 SCF/day (10.39 x 10^9 Btu/hr)

	10^9 Btu/hr
Coal dryer	0.33
Slurry pump	0.04
Recycle oil heater	0.06
Oxygen heater	0.01
Gas purification	0.80
Gasifier steam	1.48
Oxygen production	0.56
Electrical production	0.37
Low temperature heat for water treatment and other uses (arbitrary)	0.29
Driving energy required	3.89
Less steam raised in process	2.12
	1.77
Boiler stack loss	0.30
Net heat required from additional fuel	1.07

(3) Gas purification was by the Selexol type process as discussed in Section 8 (steam requirement is 28,400 Btu/lb mole CO_2 absorbed).

(4) The energy for oxygen production is the energy to compress air to 90 psia and oxygen from 15 psia to 1250 psia.

The steam raised in the process can all be used, and 1.97×10^9 Btu/hr of additional fuel must be burned to drive the plant. As shown on Table 5-8, the plant conversion efficiency is about 71.2 percent and 4.08×10^9 Btu/hr low level heat is unrecovered. To determine the cooling water requirement the ultimate disposition of the unrecovered heat was then investigated.

5.4 ULTIMATE DISPOSITION OF UNRECOVERED HEAT, WYOMING

The ultimate disposition of unrecovered heat is shown on Table 5-9. From the table, using the discussion of Section 10, the cooling water requirement will be calculated. Table 5-9 is taken directly from Tables 5-5, 5-6 and 5-7.

TABLE 5-8. HYGAS PLANT USING WYOMING COAL: OVERALL HEAT BALANCE

Basis: 250×10^6 SCF/day (10.09×10^9 Btu/hr)

	10^9 Btu/hr
IN	
Coal to gasification	12.20
Coal to boiler	1.97
	14.17
OUT	
Product gas	10.09
Unrecovered heat	4.08
	14.17
Plant conversion efficiency	71.2%

5.5 WATER FOR FLUE GAS DESULFURIZATION

When as-received Wyodak coal of the composition shown on Table 5-3 is burnt, it produces about 1.3 lb SO_2 per 10^6 Btu. Burning North Dakota lignite of the composition shown on Table 5-9 may result in about 1.7 lb SO_2 per 10^6 Btu. Burning New Mexico subbituminous coal of the composition shown on Table 5-9 may result in about 1.5 lb SO_2 per 10^6 Btu. We assume the flue gas will be desulfurized. From formulas (3) and (4) of Section 4.3, 0.49 lb water will be consumed per 1 lb of Wyoming coal; 0.19 lb water will be consumed per 1 lb of North Dakota coal; and 0.51 lb water will be consumed per 1 lb of New Mexico coal. The Wyoming site burns about 212,700 lb/hr coal and consumes 104,000 lb water/hr. At North Dakota, about 356,100 lb/hr coal are burnt consuming 67,7[illegible] lb water/hr. At New Mexico about 204,600 lb/hr coal are burnt consuming [illegible],000 lb water/hr.

It is possible to gasify the coal and to remove H_2S rather than to remove SO_2 from the flue gas. The production of fuel gas, including necessary water evaporated for cooling, consumes very little water and the water required for flue gas desulfurization can be saved. However, the loss in efficiency and added cost are high and we have assumed that fuel gas is not produced.

5.6 HYGAS PROCESS AT NEW MEXICO AND NORTH DAKOTA

For this study it was not possible to ask the Institute of Gas Technology to repeat their gasifier balances for these sites. The results have, therefore, been approximated. For a first approximation the gasifier balances for Wyoming will serve for these coals if the carbon plus hydrogen (i.e., the heating value of the coal) fed to the gasifier is unaltered.

Approximate analyses of New Mexico subbituminous coal and North Dakota lignite are shown on Table 5-9. Table 5-10 shows the coal and water process streams at New Mexico and North Dakota plants. The quantities of ash residues from the gasifier were calculated from the ash content in coal at each site assuming that the composition is that shown on Table 5-3. Also shown on Table 5-10 is the estimated plant driving energy requirements at two sites.

TABLE 5-9. APPROXIMATE ANALYSES OF NEW MEXICO SUBBITUMINOUS COAL AND NORTH DAKOTA LIGNITE

	New Mexico subbituminous coal	
Coal composition, wt %	As-received	Fed to gasifier
C	53.6	62.8
H	3.9	4.6
O	11.1	13.0
N	0.9	1.0
S	0.7	0.8
Ash	13.5	15.8
Moisture	16.3	2.0
HHV (calculated)	9382 Btu/lb	

	North Dakota lignite	
Coal composition, wt %	As-received	Fed to gasifier
C	42.5	63.9
H	2.9	4.4
O	13.4	20.1
N	0.7	1.0
S	0.6	0.9
Ash	5.1	7.7
Moisture	34.8	2.0
HHV (calculated)	6925 Btu/lb	

TABLE 7-10. PROCESS COAL AND WATER STREAMS AND PLANT DRIVING ENERGY REQUIREMENTS AT NEW MEXICO AND NORTH DAKOTA

Basis: 250×10^6 SCF/day (10.09×10^9 Btu/hr)

10^3 lb/hr	New Mexico	North Dakota
As-received coal	1,300	1,752
Vaporized moisture from coal drier	190	586
2% moisture coal fed to gasifier	1,110	1,166
Steam to gasifier	1,015	1,015
Foul condensate	294	294
Clean condensate from methanator	301	301
Ash residue from gasifier	220	112
10^9 Btu/hr		
Coal drying energy	0.28	0.79
Other plant driving energy*	3.56	3.56
Total plant driving energy required	3.84	4.35
Less steam raised in process	2.12	2.12
	1.72	2.23
Boiler stack loss	0.19	0.25
Bottom ash from boiler	0.005	0.003
Net heat required from additional fuel	1.92	2.48

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* Taken from the driving energy required in Table 5-7, excluding the energy for coal drying.

These results are similar to the Wyoming plant (Table 5-7) with the exceptions of coal drying energy and boiler stack loss which were calculated for each site according to the moisture content of the as-received coal. Table 5-11 shows the thermal efficiency estimates based on the performance at the Wyoming site (see Table 5-8). Coal drying accounts for the major changes in efficiency. Also shown on Table 5-11 is the ultimate disposition of unrecovered heat at both sites. The results at the Wyoming site (Table 5-9) were used wherever applicable. Only coal drying, boiler stack loss and bottom ash from the gasifier and boiler were calculated for each site and the rest were assumed to be unchanged from site to site. Slight imbalances resulted at both New Mexico and North Dakota sites due to the simplifying assumptions.

TABLE 5-11. APPROXIMATE THERMAL EFFICIENCY AND ULTIMATE DISPOSITION OF UNRECOVERED HEAT AT NEW MEXICO AND NORTH DAKOTA

Basis: 250×10^6 SCF/day (10.09×10^9 Btu/hr)

10^9 Btu/hr	New Mexico		North Dakota	
Coal to gasification	12.20		12.20	
Coal to boiler	1.92		2.48	
Total energy input	14.12		14.68	
Less product gas HHV	10.09		10.09	
Unrecovered heat	4.03		4.59	
Approximate conversion efficiency	71.5%		68.7%	
Disposition of unrecovered heat				
Coal drying	0.21		0.66	
Heat in hot condensate	0.01		0.01	
Electricity used plus slurry pump dissipation	0.10		0.10	
Boiler stack loss	0.19		0.25	
Combustibles lost in purification	0.80		0.80	
Total Direct Loss		1.31		1.82
Air cooling of plant process stream		0.55		0.55
Wet cooling of plant process stream		0.23		0.23
Hot ash from gasifier		0.72		0.36
Bottom ash quench from boiler		0.005		0.003
Total steam turbine condensers		0.65		0.65
Total compressor interstage cooling		0.16		0.16
Acid gas removal regenerator condensor		0.80		0.80
		4.43		4.57
Unaccounted energy dissipation		(0.40)		(0.02)
		4.03		4.59

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SECTION 6

SYNTHANE PROCESS

6.1 INTRODUCTION AND SUMMARY OF RESULTS

The Synthane process for the production of high-Btu pipeline gas is being developed by the Bureau of Mines.[1-9] A laboratory scale gasifier has been in operation at Bruceton, Pennsylvania. It is a 4-inch diameter tube inside a 10-inch diameter shell.[1] A pilot plant capable of handling 75 tons per day of coal or lignite at 1,000 psig is being started up at Bruceton. The pilot plant gasifier is 3 ft (inside diameter) by about 90 ft high.[2]

Run-of-mine coal is crushed to minus 3/4-inch in hammer mills. The crushed coal is further reduced in ball mills so that at least 70 percent will pass through 200 mesh. The pulverized coal is fed to the pretreater through lock hoppers. Coals which tend to cake when heated in a hydrogen atmosphere are pretreated in a fluid bed pretreater by reacting at 750-800°F with about 12.5 percent of the total steam and oxygen fed to gasification. Coal overflows from the pretreater and enters the gasifier which is a single stage fluid bed reactor operating between 1400 and 1800°F. Gas leaves through an internal cyclone which returns solid fines to the fluidized bed via a dip leg (see Figure 6-1).

About 30 percent of the carbon fed to the gasifier is not gasified. It is released as char and tar. Part of the char is burnt to provide power for running the plant. We find that all of the char is not needed and so some is presumed to be sold.

The Synthane process has been chosen for a detailed study at the Wyoming site only. The gasifier details have been taken from the Bureau of Mines design[3] and the rest of the plant has been calculated so as to be compatible

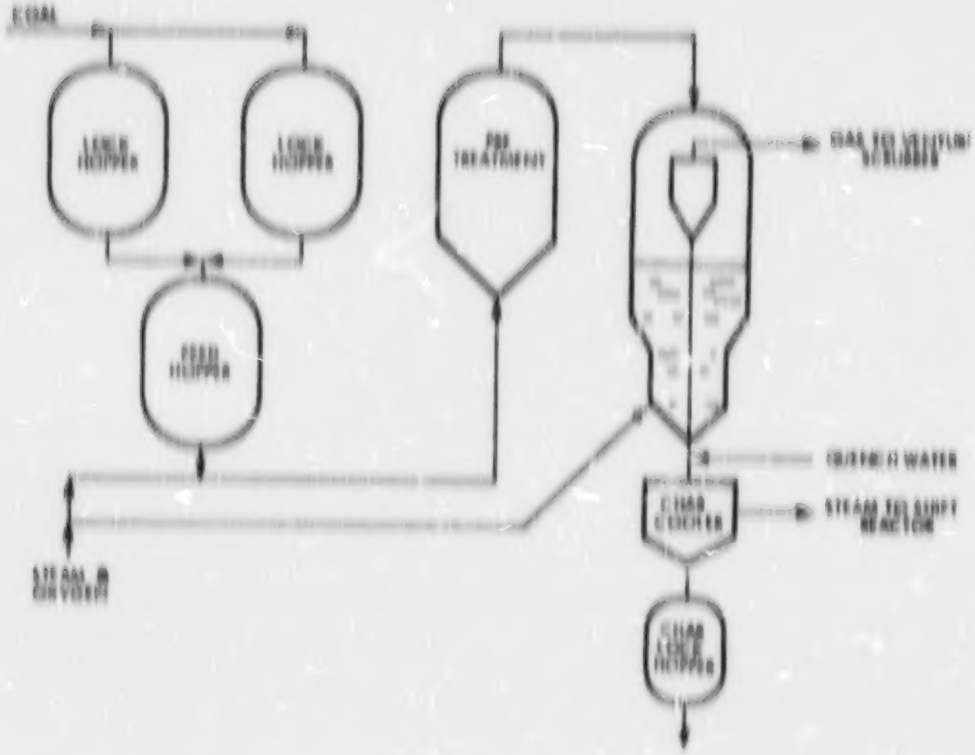
COAL
LOCK HOPPER
LOCK HOPPER
FEED HOPPER
PRE TREATMENT
GAS TO VENTURI SCRUBBER
QUENCH WATER
CHAR COOLER
STEAM TO SHIFT REACTOR
STEAM & OXYGEN
CHAR LOCK HOPPER

Figure 6-1. Flow diagram for Synthane gasifier.

with the design procedure used for the Hygas process and to minimize water consumption. The water equivalent hydrogen balance, which gives all process water streams, is shown on Table 6-1. Table 6-2 shows the ultimate disposition of unrecovered heat from which the cooling water requirements will be calculated. The analysis of the coal used is shown on Table 6-3. The details of the design from which Tables 6-1 and 6-2 were made will now be given.

6.2 MATERIAL BALANCE

The gas production train is shown on Figure 6-2. Stream compositions are shown on Table 6-4. The streams into and out of the gasifier are taken from Reference 5. The other streams have been calculated. The shift equilibrium temperature was taken as 750°F as in the Hygas design.

The Bureau of Mines design[5] shows water added to the circulating scrubber water and recovered in Stream 5. This will dilute Stream 5 which is foul water. It is not certain that this is necessary and it has not been done in this design. If it is necessary, water streams 8 and 9 should be used for this purpose.

The ash quench system shown in Figure 6-2 is from Reference 9, not Reference 5. A small amount of the steam needed for the shift reaction is produced from dirty water rather than from boiler feed water. The char temperature is assumed reduced from about 1700°F to about 800°F.

6.3 HEAT BALANCES

The gasifier balance is shown on Table 6-5. Some steam is raised in the gasifier jacket.[5] The energy contained in the char and tar were approximated as follows: 1) the weight of char shown on Table 6-4 was given by the Bureau of Mines;[5] 2) the composition of char was as scaled from Strakey et al[9] to fit the ash weight and is shown on Table 6-6; 3) the carbon and hydrogen balances on the gasifier were then used to find the carbon and hydrogen contents of the tar; 4) the heating values of the char and tar were calculated from the composition. In fact, for our purpose, the distinction between char and

TABLE 6-1. WATER EQUIVALENT HYDROGEN BALANCE FOR SYNTHANE PLANT

Coal feed: 1,918 x 10^3 lb/hr of Wyodak seam subbituminous coal (3.5 wt. % hydrogen and 19.9 wt. % moisture) as-received. Dried to 4.3 wt. % moisture (heating value of 10,640 Btu/lb) as fed to gasifiers.

Product pipeline gas: 250 x 10^6 SCF/day with heating value of 940 Btu/SCF (92.3 vol. % methane and 1.8 vol. % hydrogen).

	10^3 lb/hr
IN	
Moisture in coal	382
Water equiv. of hydrogen in coal	604
Steam to gasifier and shift convertor	1167
	2153
OUT	
Water lost in drying coal	313
Foul condensate after scrubbing	516
Condensate after shift conversion	138
Condensate after acid gas removal	20
Clean methanation condensate	140
Water equiv. of hydrogen in by-products and lost gas	87
Water equiv. of hydrogen in product gas	920
	2134

TABLE 6-9. ULTIMATE DISPOSITION OF UNRECOVERED HEAT

Basis: 250 x 10^6 SCF/day (9.79 x 10^9 Btu/hr)

	10^9 Btu/hr	10^9 Btu/hr
Coal drying	0.42	
Heat in hot condensate water	0.14	
Losses around gasifier	0.40	
Electricity used	0.11	
Char boiler stack losses	0.34	
Combustibles lost in purification	0.10	
Subtotal - Direct losses		1.51
Air cooling of plant process streams*		1.53
Wet cooling of plant process streams*		0.28
Bottom ash quench from char boiler		0.02
Total steam turbine condensers		1.04
Total compressor interstage cooling		0.34
Acid gas removal regenerator condenser		1.01
		5.73

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* The unaccounted for loss in the gas production train balance (Table 6-7) and the heat assumed for water treatment and other uses (Table 6-8) is assumed distributed 50% to dry cooling and 50% to wet cooling, for example, the heat lost by air cooling of plant process streams is here taken to be 1.33 x 10^9 (from Table 6-7) + 0.11 x $10^9/2$ (unaccounted loss from Table 6-7) + 0.3 x $10^9/2$ (heat for water treatment and other uses from Table 6-8).

TABLE 6-1. COAL FOR SYNTHANE EXAMPLE

Wyoming coal, wt. %.

	As Received	Fed to Gasifier
C	54.0	64.5
H	3.5	4.1
N	0.8	1.0
S	0.6	0.8
O	14.1	16.8
Ash	7.1	8.5
Moisture	19.9	4.3
	100.0	100.0
HHV (Btu/lb)		10,640

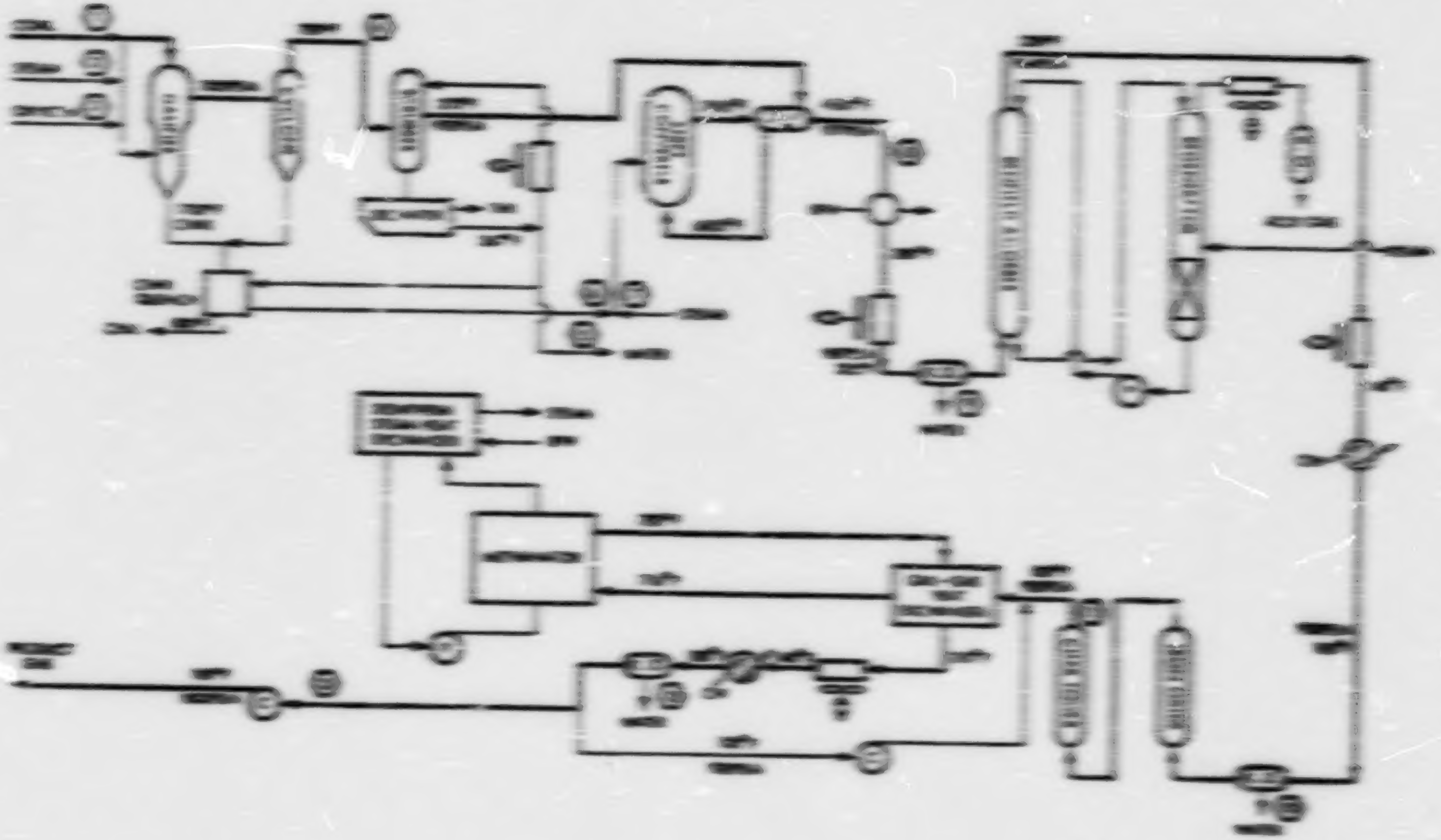

Figure 6-1. Flow diagram for Synthane process.

TABLE 6-4. STREAM COMPOSITIONS FOR SYNTHANE PLANT (SEE FIGURE 6-2)

GASIFIER FEEDS

		10^3 lb/hr
(1)	Coal	1,605
(2)	Steam	578
(3)	Oxygen	481

GASIFIER EFFLUENT

	10^3 lb/hr
Char	410

PROCESS STREAMS (10^3 moles/hr)

	(4)	(5)	(6)	(7)	(8)	(9)	(10)	(11)	(12)	(13)
CO	16.70				7.82			7.82		0.63
CO_2	25.89				34.77			1.02		1.04
H_2	16.03				24.91			24.91		0.53
CH_4	15.24				15.24			15.22		25.22
C_2H_6	1.12				1.17			1.12		
H_2O	36.41	20.60	4.27	10.51	9.36	7.68	1.09	0.05	7.76	0.03

TABLE 6-5, SYNTHANE GASIFIER HEAT BALANCE

	10^9 Btu/hr
IN	
Coal	17.08
Steam (satd. at 1000 psia)	1.12
	18.20
OUT	
Gas	12.14
Low pressure steam raised in jacket[5]	0.61
Char (before quench)	4.25
Tar	0.80
Unaccounted loss	0.40
	18.20

TABLE 6-6, CHAR ANALYSIS AND FLUE GAS DESULFURIZATION WATER

	wt. %
C	83.6
H	1.0
O	1.4
N	0.4
S	0.3
Ash	13.3
	100.0
HHV (calculated)	9800 Btu/lb

tar is not important.

A small loss was found around the gasifier. This was assumed to be directly lost to the atmosphere.

The heat balance was then extended to the complete gas production train. The heat exchangers and waste heat recovery were individually calculated. The balance (Table 6-7) shows an additional small loss which, in Table 6-2, was assigned 50 percent to dry cooling and 50 percent to wet cooling.

The driving energy required for the plant is shown on Table 6-8. In making Table 6-8 the following rules were used:

(1) Coal must be heated to 220°F and the water evaporated to dry the coal.

(2) The lock hopper compressors require 6,000 kw.[4]

(3) The steam requirement for gas purification by the Benfield process is 30,000 Btu per mole CO_2 absorbed.

(4) The energy for oxygen production is the energy to compress air to 90 psia and oxygen from 15 psia to 1015 psia.

TABLE 6-7. SYNTHANE GAS PRODUCTION TRAIN HEAT BALANCE

	10^9 Btu/hr
IN	
Coal	17.08
Steam	1.43
	18.51
OUT	
Product gas	9.79
Char	4.16
Tar	0.80
Steam produced	1.61
Combustibles lost in gas purification	0.10
Sensible heat of condensate	0.14
Loss around gasifier	0.40
Dry cooling of process streams	1.33
Wet cooling of process streams	0.07
Unaccounted loss	0.11
	18.51

TABLE 6-8. SYNTHANE PLANT DRIVING ENERGY

	10^9 Btu/hr
Coal drying	0.42
Lock hopper compressors	0.08
Gas purification	1.01
Process steam	1.43
Oxygen production	1.05
Electrical production (31,000 kw)	0.36
Low temperature heat for water treatment and other uses	0.30
Driving energy required	4.65
Less steam produced in process	(1.61)
Net heat required from fuel	3.04
Char fired boiler	
Heat recovered	3.04
Stack loss	0.34
Hot bottom ash	0.02
Char feed to boiler	3.40

All of the steam raised in the process can be usefully consumed. As shown on Table 6-8, 3.5×10^9 Btu of char (or tar) must be burnt to drive the plant. The remainder of the char and tar is available for sale. Thus, as shown on Table 6-9, the plant conversion efficiency is about 66.4 percent and 5.74×10^9 Btu/hr low level heat is unrecovered. To determine the cooling water requirement the ultimate disposition of the unrecovered heat is investigated.

6.4 ULTIMATE DISPOSITION OF UNRECOVERED HEAT

The ultimate disposition of unrecovered heat is shown on Table 6-2. From this table, using the discussion of Section 10, the cooling water requirement can be calculated. Table 6-2 is taken directly from Tables 6-5, 6-7 and 6-8.

6.5 WATER FOR FLUE GAS DESULFURIZATION

When char of the composition shown on Table 6-6 is burnt, an emission of about 0.6 lb SO_2 per 10^6 Btu will result. For this study it is assumed that desulfurization will be required. From Formula (3) of Section 8.2, 0.8 lb water will be consumed per 1 lb char. About 136,000 lb/hr char are burnt consuming 269,000 lb water/hr.

TABLE 5-9. SYNTHANE PLANT OVERALL HEAT BALANCE

	10^9 Btu/hr
IN	
Coal	17.08
OUT	
Product gas	9.79
Char	4.16
Tar	0.80
(Less char feed to boiler)	(1.40)
Unrecovered heat	3.73
	17.08

Plant conversion efficiency 66.4%

REFERENCES SECTION 6

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2. U.S. Department of the Interior, "An Economic Evaluation of SYNTHANE Gasification of Pittsburgh Seam Coal at 1000 psia Followed by Shift Conversion, Purification, Single-Stage Tube Wall Methanation and Pollution Control," Report No. 74-11, Bureau of Mines, Morgantown, W. Virginia, 1974.

3. Forney, A. J., Haynes, W. P., Elliott, J. J., Gasior, S. J., Johnson, G. E., and Strakey, J. P., Jr., "The SYNTHANE Coal-to-Gas Process," IGT Symposium on Clean Fuels from Coal, Institute of Gas Technology, Chicago, Illinois, Sept. 10-14, 1973.

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6. Gasior, S. J., Forney, A. J., Haynes, W. P. and Kenny, R. F., "Fluidized Bed Gasification of Various Coals," Chemical Engineering Progress, 71, No. 4, 89-92, 1975.

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8. Forney, A.J., Haynes, W. P., Gasior, S. J., Johnson, G. E. and Strakey, J. P., Jr., "Analyses of Tars, Chars, Gases, and Water Found in Effluents from the SYNTHANE Process," Symposium Proceedings: Environmental Aspects of Fuel Conversion Technology (May 1974, St. Louis, Missouri), Environmental Protection Agency, EPA-650/2-74-118, 1974.

9. Stickey, J. P., Jr., Forney, A. J. and Haynes, W. P., "Effluent Treatment and Its Cost for the Synthane Coal-to-S.N.G. Process" presented at American Chemical Society 168th National Meeting, Atlantic City, N. J., September, 1974; Division of Fuel Chemistry reprint Vol. 19, No. 5, page 94.

SECTION 7

SOLVENT REFINED COAL

7.1 INTRODUCTION AND SUMMARY OF RESULTS

The Solvent Refined Coal process was developed by the Pittsburgh and Midway Coal Mining Co., and two pilot plants are in operation: at Fort Lewis, Washington and Wilsonville, Alabama. Raw coal is dried, pulverized and mixed with a coal-derived solvent boiling in the general range 550-800°F. The coal-solvent slurry is pumped together with hydrogen to 1700-2500 psi and heated to about 850°F. The coal structure is broken; a small amount of the carbon reacts with hydrogen to yield light hydrocarbons and most of the coal hydrocarbon dissolves. The solution is filtered to remove ash, pyrites and unreacted char, and the solvent is separated for reuse by distillation under vacuum. The Solvent Refined Coal so produced has a fusion temperature in the range 350-450°F, has less than 0.5 percent ash and is low enough in sulfur to give 0.65 to 1.1 lb $SO_2/10^6$ Btu.

The Solvent Refined Coal process (SRC) has been chosen for detailed study. Since SRC is made by the action of hydrogen on coal, the production of hydrogen must be part of the plant design. Hydrogen is not made in the pilot plants, it is bought. We have not found an integrated plant design suitable for our purposes and so have made our own.

The plants have been sized to yield 10,000 tons SRC/day, that is 3.2×10^{11} Btu fuel/day at 16,000 Btu/lb. This is similar in size to a 50,000 bbl/day synthetic oil plant yielding about 3.2×10^{11} Btu fuel/day. The plant produces more fuel than a standard SNG plant yielding about 2.4×10^{11} Btu/day. (Upon completion of the calculation it was found that the plant in North Dakota would yield only 9,565 tons SRC/day because some of the product had to be burnt to drive the plant. For ease of understanding and comparison between sites, the calculation tables were not altered. The summary tables, however, have been scaled to 10,000 tons/day at all sites. The basis is shown on every table.) For plants of this size the process water streams are summarized on Table 7-1. The stream called "foul water from the dissolving section" is as found in the material balance calculations. These streams may in fact be bigger, as discussed in Section 7.4. Table 7-2 shows the ultimate disposition of unrecovered heat in the plants. From this table and the discussion on cooling in Section 10 will be derived the cooling requirements listed in Section 13.

7.2 DESIGN PROCEDURE

Most of the experimental work has been done on bituminous coals from Pittsburgh, Kentucky and Illinois.[1-7] Table 7-3 shows three coal analyses and three average SRC analyses derived from these coals. Very little work has been done on solvent refining a Baukol Noonan Mine, North Dakota Lignite and an Elkol Mine, Wyoming Subbituminous.[7] These experiments were in a small laboratory bench reactor; the solvent was not in balance and the analyses of the SRC are only suggestive of what might be obtained on a larger scale. However, the SRC derived from the Western coals seems very similar to that derived from Eastern coals. In fact, the SRC does not differ importantly from coal to coal and, based on the various references, the analysis shown on Table 7-3 has been assumed for all three of the coals being considered here.

An alternative process is under study, particularly as "Project Lignite" at the University of North Dakota.[8] In this process carbon monoxide or synthesis gas ($CO + H_2$) is used to dissolve the coal instead of hydrogen. Water is used (with lignite this may be the coal moisture) and the shift gas reaction, $CO + H_2O \rightarrow H_2 + CO_2$, occurs in the dissolver probably catalyzed by coal mineral. It is this process which was studied by Ralph M. Parsons Co.[9] and Jahnig[10] who, in addition, designed for one third of the SRC product to be given additional hydro-treatment to further reduce sulfur. Jahnig's study is not directly comparable to this design.

TABLE 7-1. TOTAL PLANT PROCESS WATER STREAMS

Basis: 10,000 tons SRC/day at all sites.

	Wyoming		New Mexico		North Dakota	
	10^6 gal per day	gals per 10^6 Btu*	10^6 gal per day	gals per 10^6 Btu*	10^6 gal per day	gals per 10^6 Btu
IN						
Steam and boiler feed water to: Process	1.30	4.06	1.12	3.50	1.79	5.59
Acid gas removal	0.76	2.37	0.72	2.25	0.93	2.90
	2.06	6.43	1.84	5.75	2.71	8.49
OUT						
Foul water from dissolving section	0.61	1.91	0.42	1.31	0.78	2.4
Condensate from acid gas removal	0.76	2.37	0.72	2.25	0.93	2.90
Medium quality condensate from gasification section	0.47	1.47	0.46	1.44	0.51	1.60
Clean condensate from reformer section	0.25	0.78	0.14	0.44	0.51	1.59
	2.09	6.53	1.74	5.44	2.73	8.52
Net water produced	0.03	0.10	(0.10)	(0.31)	0.01	0.03

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[*] Based on 13,340 Btu/hr as SRC only

TABLE 7-2. ULTIMATE DISPOSITION OF UNRECOVERED HEAT

Basis: 10,000 tons SRC/day ($13,340 \times 10^6$ Btu/hr) at all sites.
Units: 10^6 Btu/hr

	Wyoming		New Mexico		North Dakota	
Stack losses + coal drying	750		670		1210	
Losses around filter & dissolver	320		360		360	
Sensible heat of SRC	120		120		130	
Electricity used + slurry pump heat dissipated	70		80		80	
Other losses[a]	90		80		110	
Subtotal - Direct losses		1350		1310		1890
Air cooling of plant process streams		860		810		1010
Wet cooling of plant process streams + other allowance[a]		210		180		260
Ash quench		70		150		70
Total drive turbine condenser losses		670		640		780
Total compressor interstage cooling losses		150		140		180
Acid gas removal regenerator condenser		270		250		320
Error		(10)		(20)		(40)
Total unrecovered heat	3,570		3,460		4,470	

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[a] The energy for wastewater treatment and other low-level uses, shown on Table 7-11, has been distributed 50% to direct losses and 50% to wet cooling.

TABLE 7-1. ANALYSIS OF COAL AND SOLVENT REFINED COAL

(Analyses in wt. % for dry materials.)

	Pittsburgh[5]		Illinois[5]		Kentucky[4]	
	Coal	SRC	Coal	SRC	Coal	SRC
C	75.1	88.4	70.8	87.1	72.9	88.5
H	5.1	5.5	5.1	5.6	4.8	5.1
N	1.3	1.7	1.3	1.6	1.2	1.8
O	7.6	3.3	8.7	4.6	10.3	3.7
S	2.6	0.9	3.3	0.9	3.5	0.8
Ash	8.2	0.1	10.8	0.1	7.3	0.1
HHV(Btu/lb)		16,000		16,000		16,000

Western Coals

	New Mexico	Wyoming	North Dakota Lignite	SRC (assumed)
C	61.9	67.7	65.2	87.8
H	4.7	5.0	4.4	5.3
N	1.1	1.0	1.1	1.2
O	13.2	18.1	20.5	5.0
S	0.9	0.6	1.0	0.5*
Ash	16.2	7.4	7.8	0.2
HHV (Btu/lb)	11,180	11,590	10,620	16,000
Moisture as received.	16.3	17.9	30.6	

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* Somewhat lower when North Dakota lignite is used because less of the sulfur in the coal is organic.

The dissolving section of the plant, based mostly on the pilot plant design, is shown in simplified form in Figures 7-1 and 7-2. The plant water requirements were obtained as follows.

(1) From pilot plant results a set of rules was formulated which gives the material balance around the dissolving section of the plant.

(2) The carbonaceous filter residue is gasified to produce as much hydrogen as possible.

(3) The remaining hydrogen is produced by reforming some of the product gas.

(4) Approximate heat balances have been made around the gasification section, reforming section and dissolving section.

(5) The energy needed to drive the plant was estimated; mechanical loads (compressors, electricity generation), acid gas removal, water treatment and other loads were estimated. It was assumed that the required energy, not recovered in waste heat recovery units, would be obtained by burning product gas or oil. The quantity of gas or oil sold would then be determined and the approximate thermal efficiency of the plant stated.

(6) Finally, the points of loss of unrecovered heat have been tabulated so that the cooling water requirement could be calculated in Section 10.

The calculations showed that North Dakota lignite has such a high moisture and oxygen content there was not enough gas and oil to drive the proposed plant and some of the SRC must be burned. The addition of coal to the gasifier to produce the extra driving energy was not studied, although this should probably be done. In reading the following tables please note that the basis is shown on every table.

7.3 MATERIAL BALANCE ON DISSOLVING SECTION

Product yields for Eastern coals are generally reported as fractions of the moisture- and ash-free coal. Because of the high oxygen contents of Western coals, yields are based on carbon. Based on the published experimental results,[6] we have formulated the following rules for material balances in the dissolving section of the plant.

(1) 70 percent of the carbon in the coal appears as carbon in the SRC

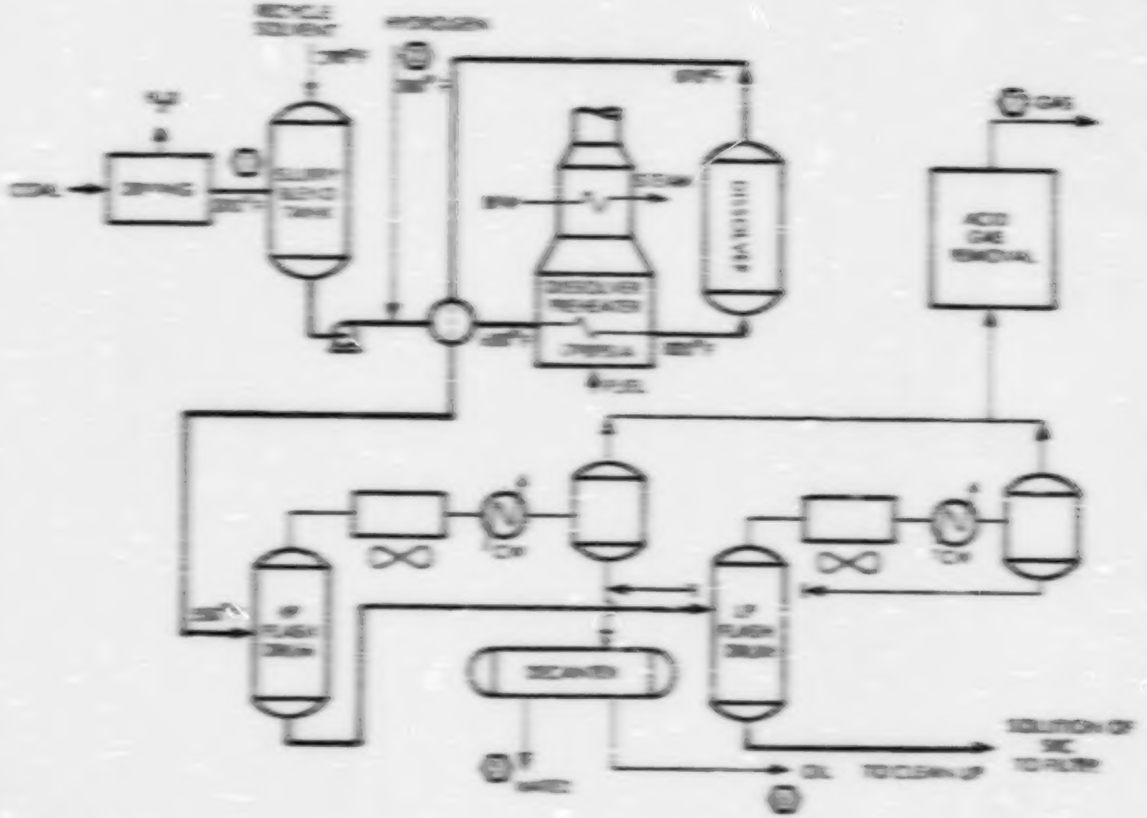
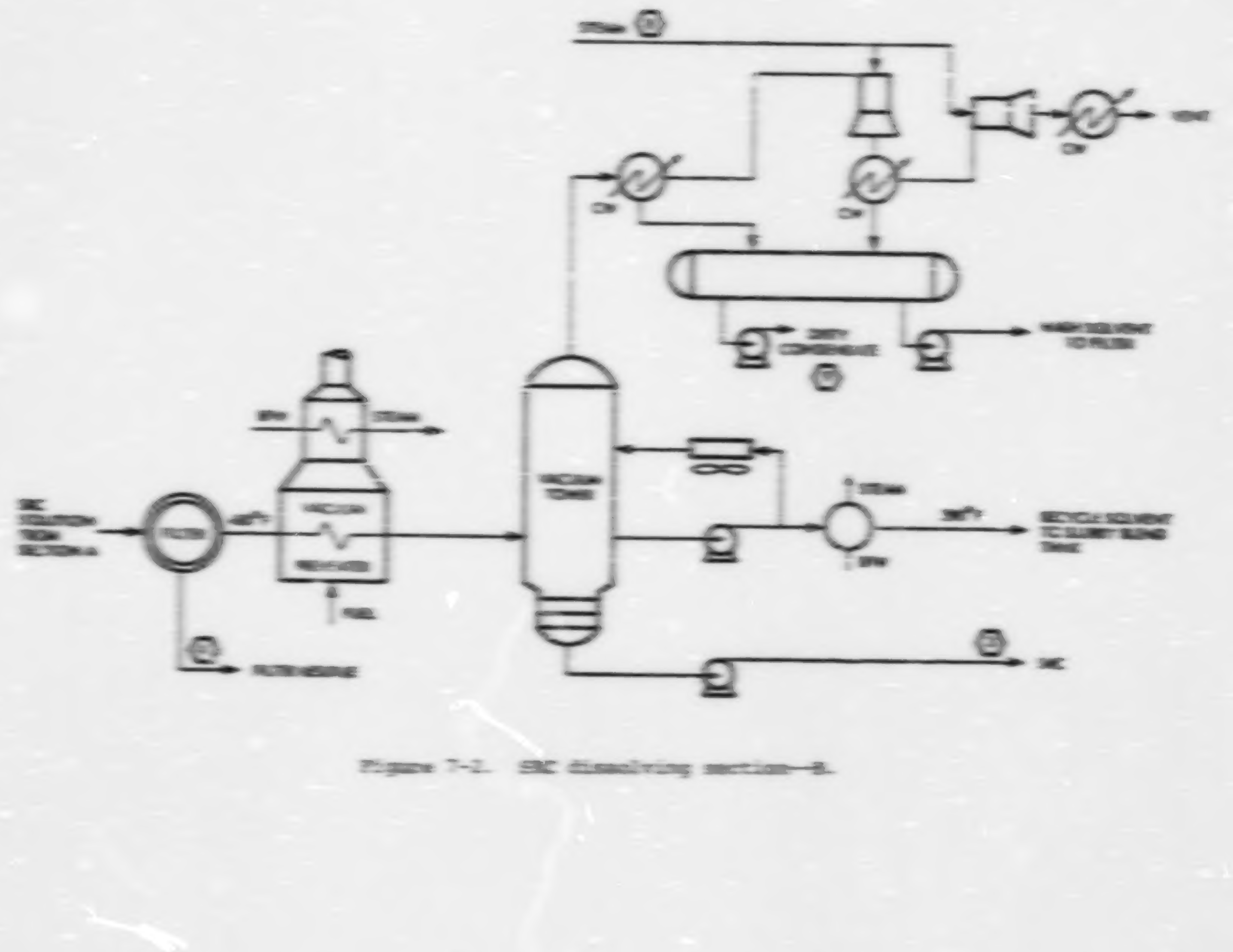

COAL
DRYING
SLURRY BLEND TANK
RECYCLE SOLVENT
HYDROGEN
DISSOLVER PREHEATER
STEAM
FUEL
DISSOLVER
ACID GAS REMOVAL
GAS
HP FLASH DRUM
LP FLASH DRUM
CW
CW
DECANTER
WATER
OIL TO CLEANUP
SOLUTION OF SRC TO FILTER

Figure 7-1. SRC dissolving section—A.



SRC SOLUTION FROM SECTION A
FILTER
VACUUM HEATER
BFW
STEAM
FUEL
FILTER RESIDUE
VACUUM TOWER
STEAM
CW
CW
CW
VENT
DIRTY CONDENSATE
WASH SOLVENT TO FILTER
STEAM
BFW
RECYCLE SOLVENT TO SLURRY BLEND TANK
SRC

Figure 7-2. SRC dissolving section—B.

and SRC has the composition shown in Table 7-3.

(2) 14 percent of the carbon in the coal appears as carbon in light liquid hydrocarbon product of composition $CH_{1.6}$.

(3) 5 percent of the carbon in the coal appears as gaseous hydrocarbon product of composition $CH_{3.7}$ (about 75 percent CH_4 and the balance higher hydrocarbons).

(4) 1 percent of the carbon in the coal appears as CO_2.

(5) 10 percent of the carbon in the coal appears as carbon in undissolved residue.

(6) The ratio O/C in the undissolved residue is the same as in the coal. The balance of the oxygen appears as water.

(7) All of the sulfate sulfur stays in the mineral residue. 50 percent of the pyritic sulfur is reduced to H_2S and the balance appears in the ash. 60-70 percent of the organic sulfur is reduced to H_2S and the balance is distributed between the SRC and undissolved residue.

(8) Nitrogen from the coal appears in the SRC and the undissolved residue, with the balance appearing as ammonia. The ratio N/C is the same in the coal and in the undissolved residue.

(9) Hydrogen is supplied as required and 10 percent of the feed hydrogen does not react.

Application of these rules gives the material balances presented on Tables 7-4 through 7-6. On these tables stream numbers from Figures 7-1 and 7-2 have been entered. For Stream 2 only the hydrogen content has been stated. In fact, the hydrogen streams produced by gasification and reforming contain only about 85 percent hydrogen with CO, CO_2 and CH_4. These extra gases are assumed to leave the dissolving section with the gas of Stream 7.

7.4 EFFLUENT WATER

The water stream shown on Tables 7-4 through 7-6 is possibly low for the following reasons: 1) coal will probably still contain 0.5 percent moisture when fed to the dissolver and this moisture may be recovered as dirty water; 2) these designs show between 58 percent and 69 percent of the oxygen in the coal converted to water. Coals having a lower oxygen content may have up to

TABLE 7-4. OVERALL MATERIAL BALANCE FOR DISSOLVING SECTION OF THE PLANT, WYOMING COAL

Basis: 10,000 tons SRC/day; (13,340 x 10^6 Btu/hr)

Units: 10^3 lb/hr

IN	Total	C	H	N	O	S	Ash
1. Coal, dry	1543	1045	77.2	15.4	279	12.1*	114
2. Hydrogen	38		38				
TOTAL	1581	1045	115	15.4	279	12.1	114

OUT	% Coal	Total	C	H	N	O	S	Ash
3. SRC	54	834	732	44.2	10.0	41.7	4.2	1.7
4. Filter Residue	16.5	255	104	7.7	1.5	28	1.5	112.3
5. Water	13	204		22.7		181		
H_2S	0.5	7		0.4			6.6	
NH_3	0.3	5		0.8	3.9			
6. Light oil	11	166	146	19.5				
7. Gaseous hydrocarbon	4.5	68	52.3	16.1				
CO_2	2.5	38	10.5			27.9		
Unconsumed hydrogen	0.3	4		3.8				
TOTAL	102.6	1581	1045	115	15.4	279	12.1	114

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* 6.4% sulfate, 22.6% pyritic, 71% organic.

TABLE 7-5. OVERALL MATERIAL BALANCE FOR DISSOLVING SECTION OF THE PLANT, NEW MEXICO COAL

Basis: 10,000 tons SRC/day (11,340 x 10^6 Btu/hr)

Units: 10^3 lbs/hr

	Total	C	H	N	O	S	Ash
1. Coal, dry	1635	1045	76.8	18.0	216	14.7[*]	265
2. Hydrogen	31		31.2				
TOTAL	1666	1045	108	18.0	216	14.7	265

	% Coal	Total	C	H	N	O	S	Ash
3. SRC	51	834	732	44.2	10.0	41.7	4.2	1.7
4. Filter Residue	24.5	401	104	7.7	1.8	21.6	2.7	263.3
5. Water	8.6	140		15.6		125		
H_2S	0.5	8		0.5			7.8	
NH_3	0.5	8		1.3	6.2			
6. Light oil	10.2	166	146	19.5				
7. Gaseous Hydrocarbon	4.2	68	52.3	16.1				
CO_2	2.3	38	10.5			27.9		
Unconsumed hydrogen	0.2	3		3.1				
TOTAL	102.0	1668	1045	108	18.0	216	14.7	265

[*] Assume distributed as Wyoming coal, see footnote to Table 7-4.

TABLE 7-6. OVERALL MATERIAL BALANCE FOR DISSOLVING SECTION OF THE PLANT, NORTH DAKOTA LIGNITE

Basis: 5,565 tons SRC/day* (12,750 Btu/lb)

Units: 10^3 lb/hr

IN	Total	C	H	N	O	S	Ash
1. Coal, dry	1603	1045	70.5	17.6	329	16.0**	125
2. Hydrogen	52		52.2				
TOTAL	1655	1045	122.7	17.6	329	16.0	125

OUT	% Coal	Total	C	H	N	O	S	Ash
3. SRC	51.1	833	732	44.2	10.0	41.7	3.5	1.7
4. Filter Residue	17.1	274	104	7.7	1.8	32.9	3.9	123.3
5. Water	15.9	255		28.5		226.5		
H_2S	0.6	9		0.5			8.6	
NH_3	0.4	7		1.2	5.8			
6. Light Oil	10.4	166	146	19.5				
7. Gaseous hydrocarbon	4.2	68	52.1	16.1				
CO_2	2.4	38	10.5			27.9		
Unconsumed hydrogen	0.3	5		5.2				
TOTAL	102.6	1655	1045	122.7	17.6	329	16.0	125

---

* Of the SRC produced in the dissolving section some is burned as plant fuel.

** 1.0% sulfate; 44% pyritic; 55% organic

85 percent of the oxygen converted to water. For these reasons, in sizing the water treatment plant this particular water stream will be assumed to have a maximum flow of:

	10^3 lb/hr	10^6 gal/day
Wyoming	275	0.8
New Mexico	215	0.6
North Dakota	323	0.9

The effluent water will contain about 0.8 percent organic carbon as 1 percent phenol (about 3 percent COD) or about 2.2 × 10^3 lb carbon/hr. The material balances are limited to this accuracy.

The rate of production of ammonia is very sensitive to the nitrogen content of the SRC. The nitrogen content of SRC was estimated to be 1.2 percent. This is lower than that found with Eastern coals and was chosen because these Western coals have a lower nitrogen content. Should the choice be wrong and should the nitrogen content of SRC be 1.6 percent, as with Eastern coals, the ammonia production might be altered as follows:

	10^3 lb/hr ammonia	
	1.2% N in SRC	1.6% N in SRC
Wyoming	6.7	8.7
New Mexico	7.5	9.5
North Dakota	7.0	9.0

The water treatment scheme must take into account unknown and possibly varying ammonia concentrations.

The ammonia may be assumed to dissolve in the condensed water and leave with it. Some H_2S will also dissolve. The nitrogen and sulfur contents of this water stream are measured daily at the Fort Lewis pilot plant, and Pittsburgh and Midway kindly supplied 22 measurements taken between 10/5/75 and 12/9/75. The measured nitrogen contents averaged 1.3 percent with a standard deviation of 0.7 percent. The measured ratio (moles NH_3/moles H_2S) was 2.0

with a standard deviation of 0.17. The nitrogen content of the water might vary as suggested above. However, the assumption of a molar ratio (NH_3/H_2S) of 2 in the water will be satisfactory for water treatment design. Most of the H_2S will probably dissolve and come out in the water stream, but some will always remain in the gas stream.

7.5 GASIFICATION OF CARBONACEOUS FILTER RESIDUE

The filter residue is a fine powder with a high ash content. The Koppers-Totzek gasifier has been taken to produce hydrogen from this material because this gasifier has proven usefulness on related materials. This gasifier is described in Section 4.10 where the rules used to obtain the gas composition leaving the gasifier are listed.* A simplified sketch of the equipment is in Figures 7-3 and 7-4, and the stream compositions are shown on Table 7-7. Streams 10, 11 and 12 follow from the gasifier rules used. The differences between coals are small and are mostly due to changes in oxygen content. The ash content has only a small effect on the material balance, although the ash content does affect the thermal balance discussed below. For Navajo coal, which gives about 66 percent ash in the residue, slag carries away about 8 percent of the higher heating value of the residue.

Stream 14 was set at 15 × 10^3 moles/hr; the shift reactor exit gases were calculated as though they were in equilibrium at 750°F (K_p = 11.8) and so Streams 15 and 16 were recorded. The acid gas removal section was taken to remove 90 percent of the CO_2 fed to it.

The approximate heat balances are presented in Table 7-8. Minor quantities, such as the sensible heat of influent and effluent streams (other than slag), are nearly in balance and have been omitted. The assignment of

---

*Oxygen feed, lb/lb (carbon + hydrogen) = 1.06
Steam feed, lb/lb (carbon + hydrogen) = 0.223
Composition of gases leaving the reactor are consistent with a shift equilibrium approximately

$$\frac{(H_2)(CO_2)}{(CO)(H_2O)} = 0.47$$

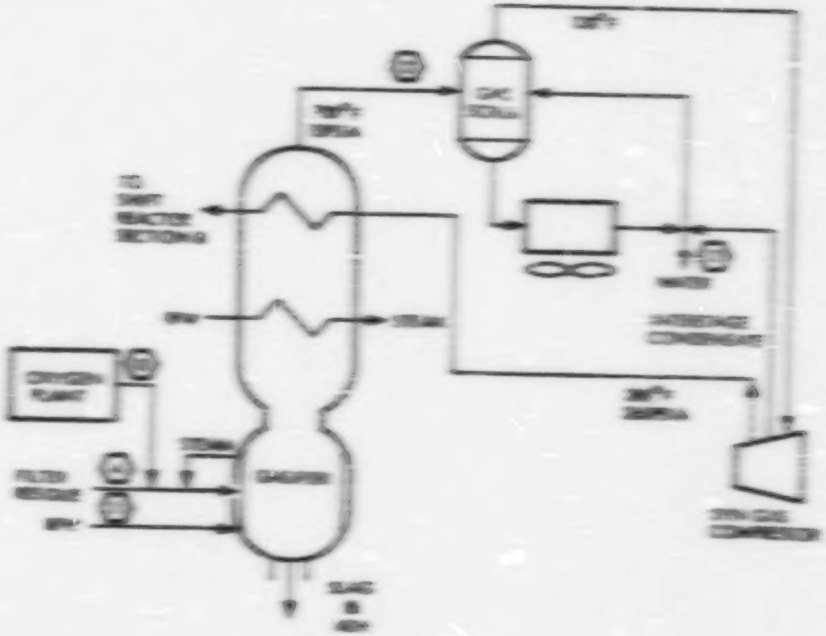
TO SHIFT REACTOR SECTIONS
OXYGEN PLANT
FILTER RESIDUE
GASIFIER
SLAG & ASH
WATER
INTERSTAGE CONDENSATE
SYN GAS COMPRESSOR

Figure 7-1. SRC hydrogen production by gasification of filter residue.

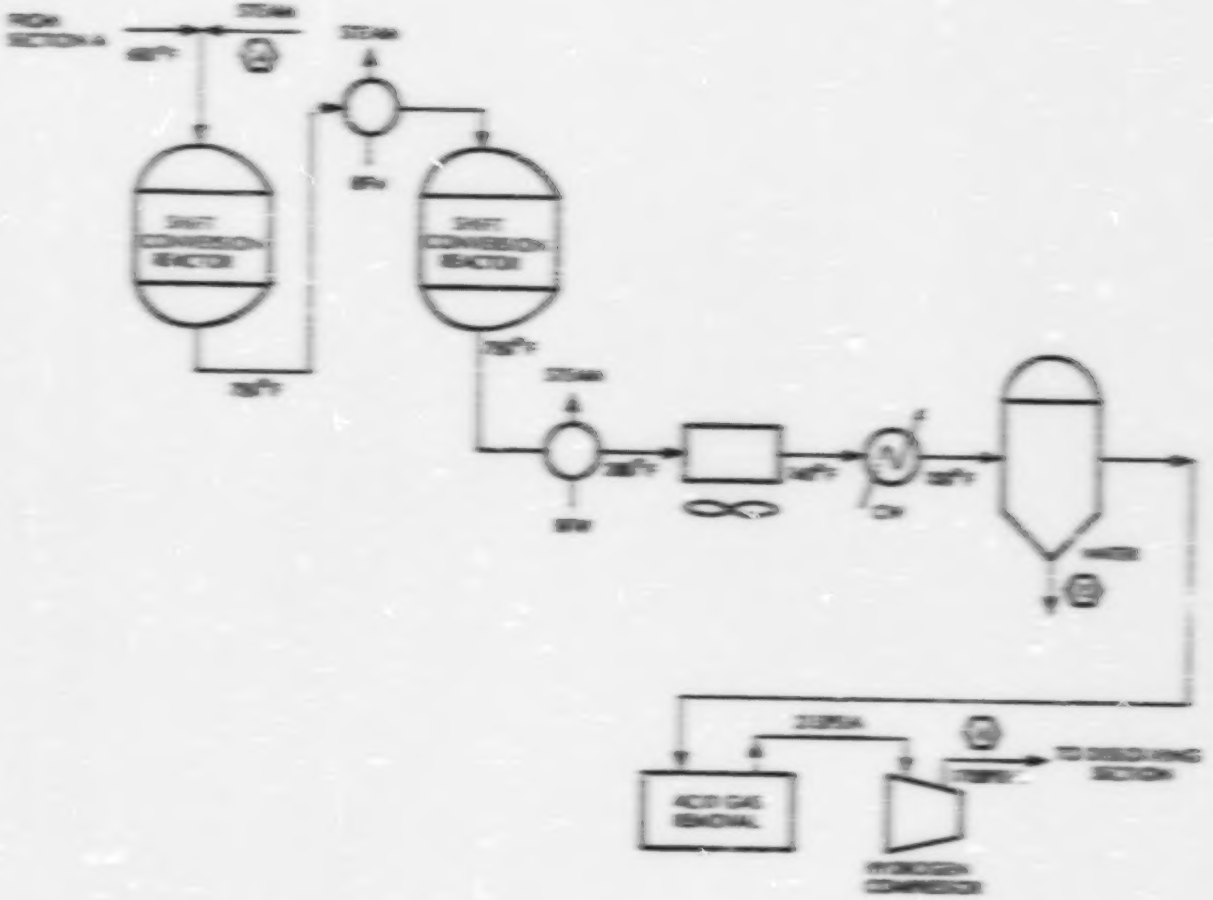
FROM SECTION A
STEAM
STEAM
BFW
SHIFT CONVERSION REACTOR
SHIFT CONVERSION REACTOR
STEAM
BFW
CW
WATER
ACID GAS REMOVAL
HYDROGEN COMPRESSOR
TO DESULFURIZING SECTION

Figure 7-4. SRC hydrogen production by gasification of filter residue—B.

TABLE 7-7. STREAMS IN THE PRODUCTION OF HYDROGEN BY GASIFICATION OF FILTER RESIDUE

Stream No.		Units	Wyoming*	New Mexico*	North Dakota**
10	O_2	10^3 lb/hr	118	118	118
11	H_2O	10^3 lb/hr	24.8	24.8	24.8
12	Raw gas	10^3 moles/hr			
	CO		7.80	7.99	7.64
	CO_2		0.86	0.68	1.03
	H_2		4.18	4.36	3.97
	H_2O		1.00	0.79	1.14
13	H_2O	10^3 lb/hr	18	14.2	20.5
14	H_2O	10^3 lb/hr	270	270	270
15	H_2O	10^3 lb/hr	146	147	148
16 Product Gas		10^3 moles/hr			
	CO		0.50	0.94	0.86
	CO_2		0.77	0.77	0.76
	H_2		11.08	11.04	10.74
16	H_2	10^3 lb/hr	22.16	22.08	21.48

---

* Basis: 10,000 tons SRC/day (11,140 x 10^6 Btu/hr)

** Basis: 9,565 tons SRC/day (12,760 x 10^6 Btu/hr)

TABLE 7-5. APPROXIMATE HEAT BALANCE FOR PRODUCTION OF HYDROGEN BY GASIFICATION OF FILTER RESIDUE

Units: 10^6 Btu/hr

Stream No.		Wyoming*	New Mexico*	North Dakota**
4	Filter residue	1780	1830	1700
14	Steam	350	350	350
	TOTAL IN	2130	2180	2050
16	Hydrogen product	1470	1470	1430
	Total steam generated	400	390	420
	Ash and clay	70	150	70
	Dry cooling load	110	110	110
	Wet cooling load	30	30	30
	TOTAL OUT	2080	2150	2050

---

* Basis 10,000 tons SRC/day (13,340 x 10^6 Btu/hr)

** Basis 9,565 tons SRC/day (12,760 x 10^6 Btu/hr)

process cooling requirements to air cooling and water cooling will be discussed in Section 10.

7.6 PRODUCTION OF HYDROGEN BY STEAM REFORMING OF GAS

The hydrogen produced by gasification of filter residue (Stream 16) is not sufficient to supply the inlet to the dissolving section, Stream 3. The extra hydrogen is made by reforming some of the gas produced in the dissolving section of the plant. The stream reforming reaction is mostly

$$CH_4 + H_2O \rightarrow CO + 3H_2$$

and it is followed by a shift reaction

$$CO + H_2O \rightarrow CO_2 + H_2$$

The reforming reaction absorbs a lot of heat and is carried out at a high temperature in a direct-fired furnace. Equilibrium is reached in both the reformer and the shift converter, and the compositions can be calculated if the temperature is known. The temperature, however, depends on the degree of reaction, and the heat and material balances are solved simultaneously. The system shown on Figure 7-5 was solved by computer program with the results shown on Tables 7-9 and 7-10. (A single gas composition was used to serve for all three coals, although the gas composition is somewhat dependent on the coal.) From these tables the important information for the three coals has been tabulated as Table 7-11.

7.7 TOTAL PLANT PROCESS WATER STREAMS

The total plant process water streams are summarized on Table 7-1. In making Table 7-1, 6,000 lb steam/hr has been used for the vacuum ejectors of the vacuum tower.[12] The condensate is added to the foul condensate of Stream 5. Steam is not required for direct addition to the tower. The steam required for acid gas removal is assumed to be used live and is shown

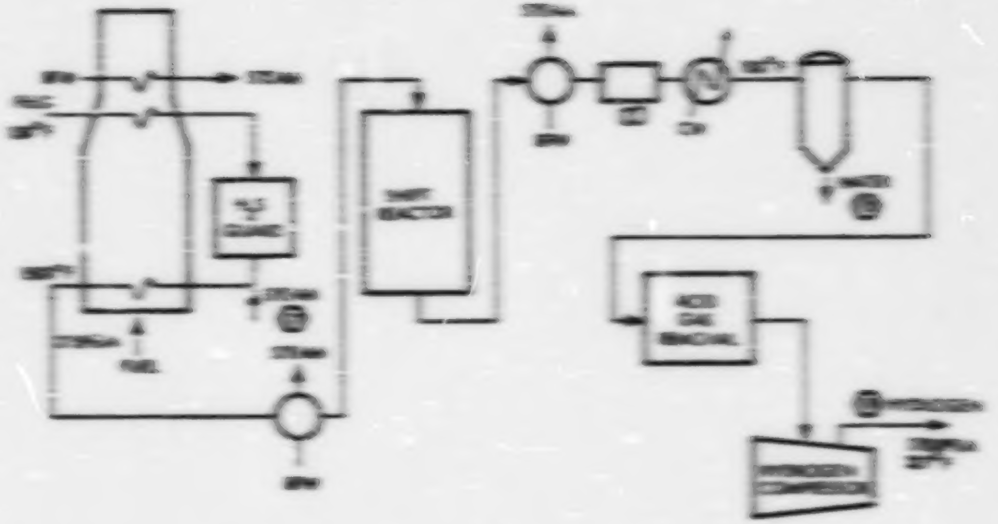
SHIFT REACTOR
ACID GAS REMOVAL
HYDROGEN COMPRESSOR
FUEL

Figure 7-1. SRC hydrogen production by reforming.

TABLE 7-9. HYDROGEN PRODUCTION BY REFORMING

Basis: 1000 moles/hr feed gas

A. Stream Flows

	Gas Feed (moles/hr)	Steam Feed (moles/hr)	Condensate Water (moles/hr)	Hydrogen Product (moles/hr)
CO				84
CO_2				46
CH_4	601			169
C_2H_6	107			0
H_2	292			2686
H_2O		2851	1643	
TOTAL	1000	2851	1643	2985

The H_2 in the product = 5.37×10^3 lb/hr.

B. Hydrogen Balance

IN	moles/hr
Gas feed	1815
Steam feed	2851
	4666

OUT	
Hydrogen product	3024
Condensate water	1643
	4667

TABLE 7-10. HEAT BALANCE ON REFORMING SECTION

Basis: 1,000 moles/hr feed gas

	10^6 Btu/hr
IN	
Reformer feed gas	337
Fuel burned	118
Steam feed	73
	528
OUT	
Hydrogen product	405
Steam produced	91
Stack loss	12
Air cooler load	16
Water cooler load	4
	528

TABLE 7-11. SUMMARY OF REFORMING SECTION

	Units	Wyoming*	New Mexico*	North Dakota**
Hydrogen required	10^3 lb/hr	15.8	9.1	30.7
Feed gas	10^3 moles/hr	2.9	1.7	5.7
Steam Feed	10^3 lb/hr	149	87	293
Condensate recovered	10^3 lb/hr	86	50	169
Reformer gas	10^6 Btu/hr	977	571	1921
Fuel	10^6 Btu/hr	342	201	673
Steam produced	10^6 Btu/hr	255	150	501
Air cooling load	10^6 Btu/hr	46	27	91
Water cooler load	10^6 Btu/hr	12	7	23

* Basis 10,000 tons SRC/day (13,340 x 10^6 Btu/hr)

** basis 9,656 tons SRC/day (12,760 x 10^6 Btu/hr)

separately. The steam requirement is 26 lb steam/mole CO_2. On Table 7-1 the results for North Dakota have been scaled to 10,000 tons SRC/day.

7.8 HEAT BALANCE ON THE DISSOLVING SECTION

An approximate heat balance on the dissolving section is given on Table 7-12. In the dissolver, chemical reactions tend to cause a rise in temperature. This rise has been taken to be 50°F as shown on Figure 7-1. This is among the higher temperature rises recorded in Reference 6. Even with this rise a loss of energy around the dissolver was found and is recorded on Table 7-12. This loss may not occur; in any event, this energy will not go to evaporate cooling water. It is the cooling water requirement which is the objective of this study.

The additional rules used to calculate Table 7-12 are:

(1) The dissolver preheater fired duty was calculated on the assumption that 2 lb of solvent are mixed with each 1 lb of dry coal to make the slurry. Hydrogen is added and the whole mass is heated through 170°F. Of the fired duty, 61 percent is used in the radiant section to heat the slurry, 29 percent is recovered as steam and 10 percent goes up the stack. This may be optimistic with regard to the steam generated.

(2) The flashed gas, water and oil are passed through an air cooler and then a water cooler in series. The gas is cooled from 550 to 100°F. The water and oil are condensed. Most of the heat removed comes from condensing the water in the flash stream, and most of this removal occurs in the air cooler. Twenty percent of the entire cooling load has been assigned to wet cooling.

(3) A loss has been assumed around the filter corresponding to a 100°F drop in temperature.

(4) The vacuum preheater is designed to heat the vacuum tower feed through 100°F and to vaporize all the solvent assuming 141 Btu/lb for a latent heat. As with the dissolver preheater, the radiant duty is 61 percent of the fired duty, 29 percent is recovered as steam and 10 percent goes up the stack. All of the vaporized solvent must be condensed, and this can be done by an air cooler.

TABLE 7-12. APPROXIMATE HEAT BALANCE ON DISSOLVER SECTION

Units: 10^6 Btu/hr

Stream No.		Wyoming*	New Mexico*	North Dakota**
1	Coal, dry	17,870	18,280	17,030
2	Hydrogen & carbon monoxide	1,640	2,160	1,740
	Fuel to dissolver & vacuum preheaters	1,720	1,810	1,300
	TOTAL IN	22,230	22,250	22,570
3	SRC	11,340	11,340	11,340
4	Filter residue	1,780	1,830	1,700
6	Oil	2,860	2,860	2,860
7	Gas (hydrocarbon + H_2 + CO)	2,170	2,080	2,460
	Steam recovered	800	840	840
	Stack losses	170	180	180
	Dry cooling load	700	670	770
	Wet cooling load	70	50	80
	Losses around filter	230	250	240
	Losses around dissolver	90	110	100
	Sensible heat in SRC	120	120	120
	TOTAL OUT	22,330	22,330	22,690

---

* Basis 10,000 tons SRC/day (13,340 x 10^6 Btu/hr)

** Basis 9,565 tons SRC/day (12,760 x 10^6 Btu/hr)

(5) The recycled solvent is cooled from 550 to 300°F in a waste heat recovery boiler.

(6) The SRC is assumed recovered as a liquid at 550°F.

7.9 PLANT DRIVING ENERGY

The auxiliary energy to drive the plant is shown on Table 7-13 and the following notes apply:

(1) The energy to dry the coal is the energy needed to vaporize the moisture and heat the coal to 220°F.

(2) The energy for acid gas removal is discussed in Section 8. It has been taken to be 28,400 Btu/mole CO_2.

(3) The electric load is 10,000 kw. The heat rate for the generator and all turbines in the plant was taken as 11,700 Btu/kw-hr, as discussed in Section 8.

(4) The energy needed to produce oxygen is the energy required to compress the equivalent weight of air to 90 psia.

7.10 THERMAL EFFICIENCY

The thermal efficiency is calculated on Tables 7-14 and 7-15.

7.11 ULTIMATE DISPOSITION OF WASTE HEAT

The ultimate disposition of waste heat is presented on Table 7-2 so that cooling water requirements can be estimated in Sections 10 and 13. About 40 percent of the unrecovered heat is lost to the atmosphere without heat transfer. About 24 percent of the unrecovered heat will be lost in dry coolers in the plant. The justification for the use of dry coolers is given in Section 10 and has to do with the high temperatures of SRC plant process streams. Whether wet or dry cooling is to be used for the other points of cooling will be discussed in Section 10 and summed up in Section 13.

TABLE 7-11. PLANT DRIVING ENERGY

Units: 10^6 Btu/hr

		Wyoming*		New Mexico*		North Dakota**
Coal drying		490		420		850
Acid gas removal (3 places)		260		250		320
Vacuum tower ejectors		10		10		10
Mechanical loads						
Electricity	120		120		120	
Oxygen plant	180		180		180	
Syn. gas compressor	260		260		260	
Hydrogen compressors (2 places)	280		230		390	
Slurry pump	110		120		120	
SUBTOTAL - Mechanical loads		950		910		1070
Water treatment plus allowance for other low level energy and losses at 10%†		170		160		220
TOTAL		1880		1750		2470

---

* Basis 10,000 tons MAF/day (11,140 x 10^6 Btu/hr)

** Basis 9,555 tons MAF/day (12,763 x 10^6 Btu/hr)

† On Table 7-2 this energy is distributed 50% to wet cooling and 50% to losses.

TABLE 7.14. PLANT FUEL REQUIREMENTS

Units: 10^6 Btu/hr

	Wyoming	New Mexico	North Dakota
Plant driving energy required	1880	1750	2470
Net steam produced in gasification section	50	40	70
Net steam produced in reforming section	50	30	100
Net steam produced in dissolving section	800	840	840
Total steam produced	900	910	1010
Fuel for driving energy	1030*	880*	1520*
Fuel for reformer	340	200	670
Fuel for dissolver preheater	680	720	710
Fuel for vacuum preheater	1040	1090	1070
Total Fuel	3090	2890	3970

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* To that part of the fuel used for steam production or superheating has been added 10% for stack losses. This has not been added to the fuel used for coal drying.

TABLE 7-15. PLANT CONVERSION EFFICIENCY CALCULATION

Units: 10^6 Btu/hr

	Wyoming	New Mexico	North Dakota
Coal feed	17,870	18,280	17,030
SRC	13,340	13,340	13,340
Oil produced	2,860	2,860	2,860
Gas + hydrogen produced	2,170	2,080	2,460
Gas reformed	(980)	(570)	(1,926)
Fuel burned in plant	(3,090)	(2,890)	(3,970)
Total product fuel	14,300	14,820	12,750
Conversion efficiency	80%	81%	75%

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SECTION 6

OTHER PROCESS WATER NEEDS

6.1 GAS PURIFICATION

The removal of hydrogen sulfide and carbon dioxide from gases[1-5] is an important consumer of energy in coal conversion plants. In this section selected processes for gas purification will be briefly discussed with the object of understanding the energy consumption, the cooling water requirement and any influent and effluent water streams required.

Most of the sulfur in the crude gas is present as hydrogen sulfide (H_2S). However, small but important amounts of carbonyl sulfide (COS) and carbon disulfide (CS_2) as well as traces of other organics including thiophene and mercaptans are often encountered. The concentration of sulfur in the crude gas depends on both the coal and gasification process and may vary from negligible to about 1 percent by volume. Acceptable concentrations in the product gas are generally about 10 ppm for low and medium BTU gas and less than about 2 ppm for pipeline gas production involving a nickel catalyzed methanation step.

Carbon dioxide (CO_2), formed in the gasifier and in the shift converter, is present in concentrations from more than 20 percent for oxygen-blown processes down to about 2 percent for hydrogen-blown or indirectly heated gasifiers. The latter concentration may be taken as the upper limit for pipeline quality gas. Carbon dioxide should not be removed from fuel gas intended, for example, for combined cycle electric generation, and its partial removal with H_2S is an efficiency penalty in the plant.[6]

Acid Gas Removal in Pipeline Gas Production

When making pipeline gas the CO_2 and H_2S must be removed. These acid gases may be removed by adsorption into an alkaline solution. One solution widely accepted is hot potassium carbonate. The approximate chemistry of adsorption is

$$K_2CO_3 + CO_2 + H_2O \rightleftharpoons 2KHCO_3$$

$$K_2CO_3 + H_2S \rightleftharpoons KHCO_3 + KHS$$

Adsorption takes place at about 270 to 300°F and at 1000 psi. The solution saturated with CO_2 and H_2S can be regenerated for reuse by reducing the pressure and boiling with little change in temperature. Regeneration reverses the chemical equations shown above. The hot potassium carbonate process is well documented.[7-10] The drawings of the Synthane plant show "Benfield type" gas purification. The operating conditions are[10]

Regenerator steam	30,000 Btu/lb mole CO_2.
Regenerator design	Closed steam boiler, condensate recovered.
Regenerator condenser	Air cooled (see Section 10). This is being practiced.
Liquid pumping energy	0.26 kw-hr/lb mole CO_2 after use of recovery turbine. This is included in the plant electrical load.

Physical adsorbents are also used for acid gas removal. The gases dissolve in the cold solvent under pressure and are driven off by release of pressure and steam stripping. Some examples of physical adsorption processes are the Rectisol processes[11] used in all Lurgi plants, the Fluor process,[12,13] the Sulfinol processes[14-16] and the Selexol process.[17,18] The Selexol process is widely used in designs and has been used for our design of the Hygas plant. Information of the sort needed is not published, and it is difficult to generalize because of the interaction between flow scheme, equipment provided and corresponding utility requirements in any particular process application. However, the following typical acid gas process design requirements were estimated for employment in general evaluation work.

Feed gas temperature	100°F.
Regenerator steam	38,400 Btu/lb mole CO_2.
Regenerator design	In the SRC plant live steam is used and the recovered water is sent to treatment. In Hygas the load on treatment would be too high. The condensed water is assumed to be reboiled in a closed steam boiler. This increases the capital cost.
Regenerator condenser	Air cooled with trim water cooled heat exchanger to reduce gas temperature to maintain water balance (see Section 10).
Liquid pumping energy	0.3 kw-hr/lb mole CO_2 after use of recovery of turbine. This is included in the plant electrical load.

Hot Gas Desulfurization

Increased attention is being given to the use of solids for high temperature bulk H_2S removal and increased overall generating plant efficiencies.[19] Among the high temperature systems under investigation are calcined dolomite panel bed filters and fly ash/iron oxide absorbents.

In the calcined dolomite system the dolomite may be in the form of a panel bed filter downstream of the gasifier.[20] These filters could operate at temperatures of 1,300 to 1,500°F and at pressures of about 300 psi and are expected to achieve 99 percent sulfur removal. The filter may be designed to simultaneously remove fume and dust. The absorbent is regenerated by reacting it with steam and CO_2 to yield H_2S at a concentration sufficient for the Claus process:

$$CaS \cdot MgO + H_2O + CO_2 \rightleftharpoons CaCO_3 \cdot MgO + H_2S$$

Theoretical steam requirements are 0.56 lbs H_2O/lb S removed. This water is released in the panel bed filter (reverse of the above equation) and will be carried up the stack with the combustion products. Design and operation considerations are discussed in Reference 20.

The Bureau of Mines is investigating the capabilities of several solid adsorbents in the temperature range 1,000 to 1,500°F.[21,25-27] They obtained H_2S removal efficiencies of 95 percent with sintered pellets of 75 percent fly ash, 25 percent Fe_2O_3. An adsorption capacity of 0.04 to 0.06 lbs sulfur per pound of mixed absorbent was obtained, and no deterioration was detected over extended absorption-regeneration cycles. Regeneration with oxygen yields a concentrated stream of SO_2 which could be used for sulfuric acid production.

8.2 FLUE GAS DESULFURIZATION

In the Hygas plant coal may be burnt for energy to drive the plant. In the Synthane plant char will be burnt. In both of these plants flue gas desulfurization is assumed to be needed. A wet desulfurization process has been selected for the design and the following procedure is used to estimate the water requirements.

In wet scrubbers, water leaves the system as vapor in the flue gas and with the waste solids as slurry.

Water in Saturated Flue Gas

The water content of saturated flue gas depends on the temperature and pressure of saturation and is given on Table 8-1.

From Table 8-1 it is clear that lack of knowledge of the pressure of saturation in the range of interest will alter the water content of saturated gas by not more than 7 percent. However, if the temperature of saturation

TABLE B-1. MOLES WATER/MOLE DRY GAS AT SATURATION

Total pressure, (psia)		14.696	15.057	15.418
(inch water gauge)		0	10	20
Temperature				
(°F)	(°C)			
120	49	0.130	0.127	0.123
130	54	0.178	0.173	0.168
140	60	0.245	0.237	0.231
150	66	0.339	0.328	0.318
160	71	0.476	0.460	0.444

is 10°F higher than was assumed, the water content of the flue gas will be about 40 percent higher than was calculated.

Most experimental scrubbers equilibrate at an exit gas temperature of 125°F. However, to best match published water consumption the conditions assumed are 120°F (49°C) and 10 inches of water gauge so that the flue gas contains 0.13 moles water per mole of dry gas. To find the actual water evaporated, the flue gas volume must be calculated.

Assuming negligible carbon monoxide and nitrogen oxides the flue gas volume is given by the formula derived on Table 8-2. The total moles of flue gas per unit weight of coal, as fired, are

$$4.76\ (1 + a)\left(\frac{C}{12} + \frac{S}{32}\right) + (3.76 + 4.76a)\left(\frac{H}{4} - \frac{O}{32}\right) \qquad (1)$$

The makeup water requirement for gas saturation, which is the water leaving in the flue gas minus the water entering in the flue gas, is in lb/lb coal as fired

$$4.76(0.13)(1 + a)\left(\frac{C}{12} + \frac{S}{32}\right)(18)$$

$$+ (0.13)(3.76 + 4.76a)\left(\frac{H}{4} - \frac{O}{32}\right)(18) - w - \frac{H}{9} \qquad (2)$$

The excess air a varies from about 0.05 to 0.2 and 0.15 has been used. If this is introduced into Formula (2), it becomes

$$\text{lb makeup water/lb coal} = 12.8\left(\frac{C}{12} + \frac{S}{32}\right) + 10.5\left(\frac{H}{4} - \frac{O}{32}\right) - w - \frac{H}{9} \qquad (3)$$

Table 8-3 is a numerical examination of Formula (3). The biggest determinant is the moisture in the coal, w .

Now let us consider water lost with the waste solids.

Water in Waste Solids

The rate of water lost with waste solids depends on the sulfur quantity and on the slurry concentration. There are two major solid products:

TABLE B-3. DETERMINATION OF FLUE GAS VOLUME

Basis: Unit weight of coal containing:

Element	Wt.	Formula	Moles
Carbon	c	C	c/12
Hydrogen	h	H_2	h/2
Oxygen	o	O_2	o/32
Sulfur	s	S	s/32
Moisture	w	H_2O	w/18

The fraction excess air is a.

Flue gas component	Moles in dry gas	Moles O_2 required
Carbon dioxide, CO_2	c/12	c/12
Water, H_2O		(h/4)-(o/32)
Sulfur dioxide, SO_2	s/32	s/32
Oxygen, O_2	$a(\frac{c}{12} + \frac{h}{4} - \frac{o}{32} + \frac{s}{32})$	
Nitrogen, N_2	$(\frac{79}{21})(1 + a)(\frac{c}{12} + \frac{h}{4} - \frac{o}{32} + \frac{s}{32})$	
Total moles	$4.76(1 + a)(\frac{c}{12} + \frac{s}{32}) + (3.76 + 4.76a)(\frac{h}{4} - \frac{o}{}$	

TABLE 5-3. CALCULATED MAKEUP WATER FOR FLUE GAS SATURATION (SEE TEXT FOR DETAILS)

	Coal	c	h	s	n	w	lb H₂O/ lb coal
1.	Wet lignite	0.45	0.03	0.15	.006	.3	0.21
2.	Medium wet lignite	0.51	0.034	0.17	.007	.2	0.38
3.	Dried lignite	0.58	0.039	0.19	.008	.1	0.55
4.	Subbituminous	0.54	0.04	0.11	.009	.25	0.49
5.	Bituminous	0.7	0.05	0.07	.04	.05	0.82
6.	Bituminous	0.7	0.05	0.07	.03	.05	0.81
7.	Bituminous	0.7	0.05	0.07	.02	.05	0.80

TABLE 5-4. CALCULATED MAKEUP WATER FOR WASTE DISPOSAL AND TOTAL WATER

		lb water/lb coal			gpm/10⁶kw		
	Coal	in solids	in flue	total	in solids	in flue	total
1.	Wet lignite	0.05	0.21	0.26	140	570	710
2.	Medium wet lignite	0.06	0.38	0.44	152	920	1070
3.	Dried lignite	0.12	0.55	0.67	212	1380	1590
4.	Subbituminous	0.08	0.49	0.57	164	1040	1210
5.	Bituminous	0.25	0.82	1.07	544	1290	[illegible]
6.	Bituminous	0.26	0.81	1.07	402	1270	[illegible]
7.	Bituminous	0.17	0.80	[illegible]	374	1250	[illegible]

	lb solid/lb sulfur	lb water/lb sulfur
$CaSO_4 \cdot 2H_2O$	5.38	1.13
$CaSO_3 \cdot \frac{1}{2}H_2O$	4.03	0.28

Assuming a given solids concentration in the waste slurry, the weight of slurry water per unit weight of sulfur can be calculated. For example, for 40 wt percent solids concentration

Solids composition	lb slurry water/lb sulfur
$CaSO_4 \cdot 2H_2O$	8.07
$CaSO_3 \cdot \frac{1}{2}H_2O$	6.05

Vacuum filtration could increase the percent solids to 60 percent and vacuum filtration plus centrifugation could raise this figure to 70 percent.[24] However, these mechanical dewatering techniques would only be practiced if transport of the sludge to distant landfill were envisaged, which is not the case for the Western sites considered in this study.

Tables 8-5a and 8-5b give the compositions in weight fractions of lime and limestone scrubber sludges.[24] (In Reference 24 the calcium sulfite was assumed to be in the crystalline form $CaSO_3 \cdot 2H_2O$. It is now generally agreed that the form in the sludges is $CaSO_3 \cdot \frac{1}{2}H_2O$. We have therefore corrected the weight fractions in Reference 25.) Also shown in these tables are the corresponding weight fractions of sulfur and water of hydration, calculated using the values given above.

From the data of Tables 8-5 the weight of solids and of the water of hydration per unit weight of sulfur for the lime and limestone processes have been calculated. These figures are

Process	lb solid/lb sulfur	lb water/lb sulfur
Lime	5.2	0.38
Limestone	6.6	0.38

TABLE 8-5a WEIGHT OF COMPONENTS OF LIME SLUDGE (DRY) AND CORRESPONDING WEIGHTS OF SULFUR AND WATER OF HYDRATION

Component	lb solid	lb sulfur	lb water
$CaCO_3$	.058	0	0
$CaSO_3 \cdot 1/2\ H_2O$	.690	.171	.048
$CaSO_4 \cdot 2\ H_2O$	.126	.023	.026
$Ca(OH)_2$	.126	0	0
Total	1.000	.194	.074

TABLE 8-5b WEIGHT OF COMPONENTS OF LIMESTONE SLUDGE (DRY) AND CORRESPONDING WEIGHTS OF SULFUR AND WATER OF HYDRATION

Component	lb solid	lb sulfur	lb water
$CaCO_3$	.367	0	0
$CaSO_3 \cdot 1/2\ H_2O$	.533	.132	.037
$CaSO_4 \cdot 2H_2O$	.100	.019	.021
$Ca(OH)_2$	0	0	0
Total	1.000	.151	.058

The unit weights of solids are reasonably close and with little error the average of the two values is representative of any wet lime, limestone or lime-limestone scrubbing process, that is, 5.9 lb solid/lb sulfur. The water of hydration can represent only a very small fraction of the total makeup water (slurry water plus water of hydration) so that this contribution is neglected and the makeup water equals the slurry water. In this case

$$\frac{\text{lb makeup water}}{\text{lb sulfur}} = 5.9\left(\frac{1 - m}{m}\right) \qquad (4)$$

where m is the weight fraction of solids in the waste (i.e., weight of solids divided by the weight of water plus solids). Note that a change to 30 percent solids from 40 percent solids makes a 56 percent increase in the water in the waste since (1 - m)/m changes from 1.5 to 2.3. A change to 50 percent solids makes (1 - m) equal to 1 and decreases the water in the waste by 33 percent.

TABLE B-6. REPORTED AND ESTIMATED WATER REQUIREMENT FOR FGD

Quantities in gpm/10^6 kw generation.

Station	% S in Coal	Water in Stack	Water in Solids	Total Water
EPA/TVA Shawnee[22]	3.4	900	510	1410
EPA/TVA[22]	3.4	850	810	1660
Cholla, Ariz. Public Serv.[22]	0.5	430	195*	630
Kaiparowits Reference 23	0.4	816	58	870
Calculated	0.4	926	55	981
Mohave, Nevada, S. Cal. Edison[20]	0	870	47 to 71	≈ 930

*Scaled to 40% solids

Reported Experience

The limited reported experience is given on Table 8-6. In the case of Kaiparowits, the composition of the coal was given and a calculated result is also presented on Table 8-6. To compare Table 8-6 with Table 8-4, the units lb water/lb coal have been converted to gpm/10^6 kw as follows. First the coal heating value is calculated from the Dulong formula:

$$\text{HHV(higher heating value)} = 14{,}540c + 62{,}000(h-o/8) + 4{,}100s \text{ Btu/lb}$$

Then, taking 10,000 Btu/kw-hr so that coal feed is 10^{10}/HHV in lb/hr, the makeup water for flue gas saturation is

$$\frac{\text{lb water}}{\text{lb coal}} \times \frac{10^{10}}{\text{HHV}} \frac{\text{lb coal}}{\text{hr}} \times \frac{1}{500} \frac{\text{gal/min}}{\text{lb/hr}} = \frac{\text{lb water}}{\text{lb coal}} \times \frac{2 \times 10^7}{\text{HHV}} \text{ gal/min}$$

The result of this calculation is shown on Table 8-4.

Comparison of Table 8-6 with Table 8-4 suggests that the estimates are high for the flue gas even though a low saturation temperature has been assumed. Nevertheless the procedure seems to yield useful estimates of water quantity.

8.3 WATER FROM DRYING COAL

In the Synthane, Hygas and SRC processes the coal must be dried before use. The question arises: Can the water be recovered? Water recovered by drying coal is quite clean as it has been vaporized and condensed under conditions such that few volatile contaminants accompany it. For an example of quantity, the water removed when North Dakota lignite is dried for feed to the SRC plant amounts to 707 x 10^3 lb/hr = 2 x 10^6 gallons/day.

We have investigated recovering water from drying coal using several different techniques and find the cost of the recovered water to lie in the range $1.30 to $1.50 per thousand gallons. In this report we have not assumed that water will be recovered, but recovery is certainly a serious possibility when water is particularly scarce.

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SECTION 9

POWER GENERATION VIA COAL GASIFICATION IN COMBINED-CYCLE POWER PLANTS

9.1 INTRODUCTION AND CONCLUSIONS

In this section the water requirements for a plant to convert coal energy to electricity are discussed. The water requirements using gasification and combined cycle generation are shown to be less than the water requirements in a standard coal fired steam-electric generating plant.

There is not yet a reason to choose combined-cycle technology because this technology today is less efficient than standard plants. However, gasification followed by combined-cycle generation is expected to improve in efficiency when designs already started are complete, and this new technology may be used in the next generation of coal fired electric plants.

For the three coals shown on Table 9-1 a gasifier and combined-cycle generating plant have been designed using cold gas sulfur removal. The resultant plant water-equivalent hydrogen balances are shown on Table 9-2 which gives the process water streams. The plant overall energy balances, from which cooling water requirements can be determined, are shown on Table 9-3. First it is interesting to compare Tables 9-2 and 9-3 with the corresponding results for a direct fired coal burning steam-electric plant.

9.2 COMPARISON WITH A COAL BURNING STEAM-ELECTRIC GENERATING PLANT

Table 9-4 shows a comparison between the usual energy balance for a 1000 megawatt coal fired generating plant and the Wyoming combined-cycle plant. The condenser cooling load is about 130 percent of the load on wet cooling

TABLE 9-1. COALS USED IN ANALYSIS OF COMBINED-CYCLE PLANTS

Basis: 100 lb dry coal

	Wyoming		New Mexico		North Dakota	
	Dry	As fired	Dry	As fired	Dry	As fired
C	67.7	67.7	64.0	64.0	65.2	65.2
H	5.0	8.4	4.7	6.9	4.4	10.4
O	18.1	44.9	13.2	30.4	20.5	67.9
N	1.0	1.0	1.1	1.1	1.1	1.1
S	0.8	0.8	0.9	0.9	1.0	1.0
Ash	7.4	7.4	16.1	16.1	7.8	7.8
	100.0	130.2	100.0	119.4	100.0	153.4
HHV (Btu/lb)	11,940		11,660		11,267	
Moisture (%)	23.2		16.3		34.8	

TABLE 9-2, COMBINED-CYCLE ELECTRICAL PLANT WATER EQUIVALENT HYDROGEN BALANCES

Basis: 10^6 kilowatts

	10^3 lb/hr		
	Wyoming	New Mexico	North Dakota
Coal, $(H_2 + H_2O)$	753	638	1003
Boiler feed water(1)	957	970	943
TOTAL IN	1710	1608	1946
As NH_3	17	26	20
As hydrogen in tar, oil, naphtha and phenol	65	60	73
Up the stack	908	897	867
Dirty condensate(2)	720	625	986
TOTAL OUT	1710	1608	1946
Net Consumption (1) - (2)	237	345	(-43)

TABLE 9-3. COMBINED-CYCLE ELECTRIC PLANT OVERALL ENERGY BALANCES

Basis: 10^6 kilowatts

	10^9 Btu/hr					
	Wyoming		New Mexico		North Dakota	
Coal		12.00		11.99		12.17
Electricity	3.41		3.41		3.41	
Tar, oil	1.85		1.72		1.98	
Subtotal fuel		5.26		5.13		5.39
Byproducts (NH_3,S)	0.13		0.19		0.16	
Stack, other loss, dry cooling, etc.	3.05		3.15		2.85	
Subtotal-losses not requiring wet cooling		3.18		3.34		3.01
Process streams cooled by water*		0.63		0.61		0.70
Ash		0.06		0.14		0.07
Steam turbine condenser		2.85		2.75		2.97
TOTAL OUT		11.98		11.97		12.14

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* Arbitrarily includes waste heat load - thus this is points 9, 21 and 23 of Figure 9-1.

TABLE 9-4. COMPARISON OF ASSUMED ENERGY BALANCE FOR A 1,000 MEGAWATT STEAM-ELECTRIC COAL FIRED GENERATING PLANT, WITH A COMBINED CYCLE GENERATING PLANT

	Coal Fired Plant		Combined Cycle Plant (Wyoming example from Table 9-3)	
	10^9 Btu/hr	%	10^9 Btu/hr	%
Coal	9.74	100	12.00	100
Electricity	3.41	35	3.41	28
Combustible byproducts	0		1.85	15
Stack losses	0.97	10		
Flue gas reheating and other plant losses	0.68	7		
Stack losses, byproducts and dry cooling load			3.18	27
Turbine condenser and other wet cooling	4.68	48	3.54	30
	9.74	100	11.98	100

TABLE 9-5. COMPARISON OF WATER FOR FLUE GAS DESULFURIZATION IN A 1,000 MEGAWATT COAL FIRED STEAM-ELECTRIC GENERATING PLANT, WITH NET WATER FOR A COMBINED CYCLE PLANT (FROM TABLE 9-2)

	10^3 lb/hr		
	Wyoming	New Mexico	North Dakota
Coal Fired Plant			
Coal fired (as received)	975	919	1,221
Makeup water for flue gas desulfurization	458	505	366
Combined Cycle Plant			
Net water consumed	217	345	(143)

in a combined-cycle plant. Table 9-5 shows the water required for flue gas desulfurization calculated by the method of Section 8.2 compared to the net water consumption in combined-cycle plants. The water requirement is more than the net water consumed in the gasifier of a combined-cycle plant. The coal burning plant is more efficient and the comparison is incomplete, but a combined-cycle plant will use less process water and less cooling water than a direct-fired plant.

9.1 DESCRIPTION OF COMBINED-CYCLE GENERATION

Figures 9-1 and 9-2 show two simplified versions of coal gasification and combined-cycle electric generating plants. They differ in the temperature at which hydrogen sulfide is removed from the low-Btu power gas. The incentive to build a combined-cycle system is that today it offers an efficiency approaching that of a coal burning steam-electric power plant, with the probability of higher efficiencies in the near future, while at the same time employing reliable methods of preventing emissions of sulfur compounds.

In the combined-cycle concept, desulfurized coal gas is burned under pressure using compressed air to support combustion. The pressurized hot combustion products are expanded through a gas turbine which drives a power generator and the compressor supplying air for fuel gas combustion and coal gasification. A pressure of about 250 psig is required at the turbine inlet, and a Lurgi pressurized gasifier has been chosen for detailed study. As discussed below, air blown Lurgi gasifiers are used and the discussions of Lurgi for SNG and Lurgi slagging are not directly applicable.

An additional decision is whether to use oxygen or air in the gasifier. One advantage of air is that the nitrogen reduces the need for excess steam to moderate the temperature at the bottom of the gasifier. Although the presence of nitrogen increases the volume of gas passing through the purification system, it is not otherwise detrimental and nitrogen will be added with excess air in the combustor if it is not already present. Studies suggest that gasification with air is more efficient for use in this application than gasification with oxygen, and air has been chosen for this study.

The remarks about air apply to a dry ash discharge. If the gasifier is

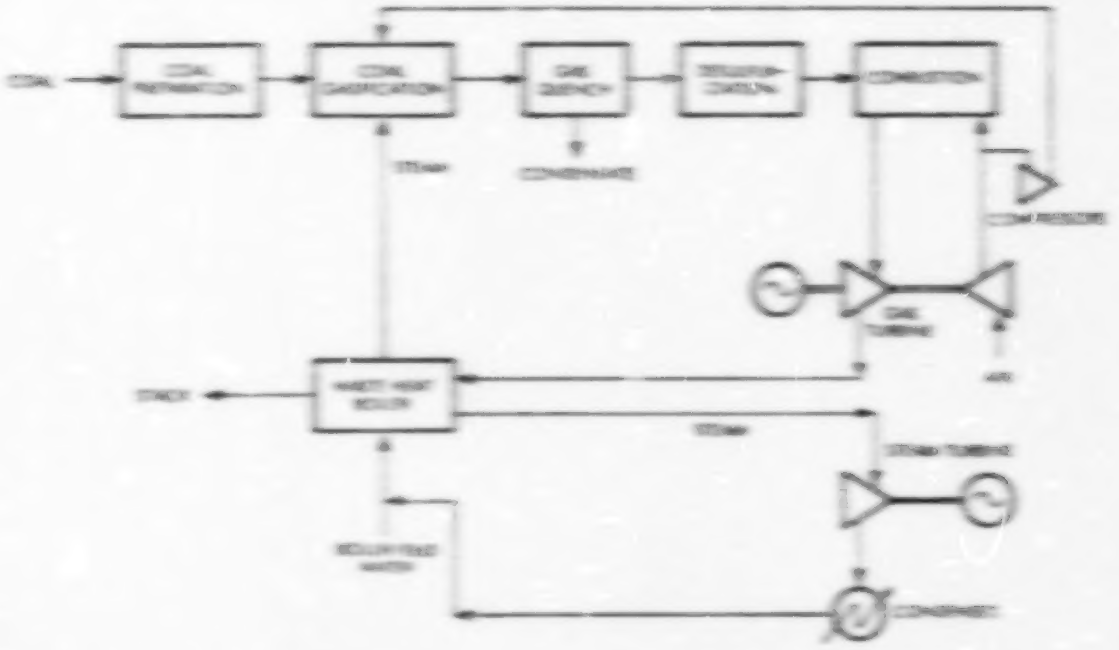

COAL
COAL PREPARATION
COAL GASIFICATION
GAS QUENCH
DESULFURIZATION
COMBUSTION
STEAM
CONDENSATE
COMPRESSOR
GAS TURBINE
AIR
STACK
WASTE HEAT BOILER
STEAM
STEAM TURBINE
BOILER FEED WATER
CONDENSER

Figure 5-2. Gasification and combined cycle generation with cold gas desulfurization.

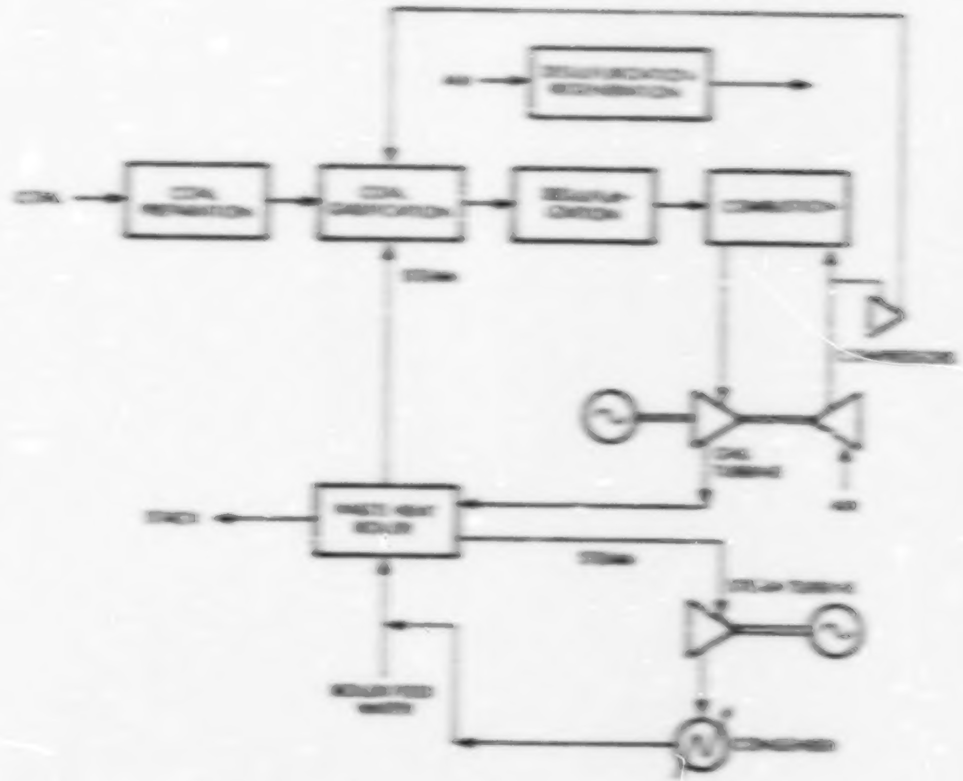

COAL
COAL PREPARATION
COAL GASIFICATION
DESULFUR-IZATION
COMBUSTOR
AIR
DESULFURIZATION REGENERATION
STEAM
COMPRESSOR
GAS TURBINE
AIR
WASTE HEAT BOILER
STACK
STEAM
STEAM TURBINE
TREATED FEED WATER
CONDENSER

Figure 9-1. Gasification and combined cycle generation with hot gas desulfurization.

operated in a slagging mode, oxygen will be used. The throughput will increase three- to fourfold and the reduced use of steam will increase the efficiency. This will more than compensate for any disadvantages that oxygen may have.[1]

Pressurized hot combustion products from burning purified coal gas are expanded through a gas turbine. As the gas passes through the turbine, it cools because some of its contained heat energy is converted to mechanical work. However, the gas leaving the turbine is at sufficiently high temperature for raising high pressure superheated steam used to generate electricity through a steam-driven turbine. Steam is exhausted from the steam turbine at a low temperature. The temperature of the gas leaving the gas turbine depends on the gas turbine inlet temperature and on the pressure expansion ratio. The capacity of the exhaust gas for producing high pressure superheated steam and the combined-cycle power generating efficiency are a function of gas turbine design.

At a given gas turbine inlet temperature and pressure, increasing the gas turbine pressure expansion ratio will tend to reduce the gas turbine exit temperature and the level of high pressure steam raised. The efficiency of the steam power cycle is reduced as steam pressure and superheat temperature fall below about 1000°F superheat. However, the efficiency is not importantly increased if steam is produced above about 1000°F. Generally, station efficiency is maximized by using the maximum practical gas turbine inlet temperature and by increasing the pressure expansion ratio as the inlet temperature increases so as to produce 1000°F superheated steam.

With increasing gas turbine inlet temperatures, less excess air is required to establish combustor exit temperature at the desired level and the air compression requirements are reduced. Station efficiency tends to be increased even though the efficiency of the gas turbine itself may decrease as more turbine cooling air is required at higher inlet temperature levels.

Increasing the gas turbine inlet temperature tends to shift the combined-cycle generating capacity towards the gas turbine, which does not require a cooled condenser, and away from the steam cycle which does require a cooled condenser. This lessens the need for cooling water.

According to information published by General Electric,[2] gas turbine design is expected to develop as follows:

> Current state-of-the-art gas turbines operate on low-Btu gas at 1950°F inlet temperature and a pressure ratio of 10:1, producing a gas turbine exit temperature of about 1065°F. The early 1980's would be about the earliest this technology can be in operation.
>
> By the mid-1980's a low-Btu gas turbine inlet temperature of 2400°F at a pressure ratio of 16:1 is anticipated. The corresponding steam conditions would be 1500 psig at the 1000°F level.
>
> Ultimately a low-Btu gas turbine inlet temperature of 3000°F at 16:1 pressure ratio is anticipated. The corresponding steam system would operate at 2400 psig 1000°F.

Based on Lurgi type gasification of a high sulfur coal, the combined cycle heat rates expected are of the following order:

Gas Turbine Inlet Temperature and Pressure Ratio	Waste Heat Steam °F/psig	Overall Heat Rate BTU (HHV)/KWH, (efficiency)
1950°F (Current) 10/1 P-ratio	900°F/1250 psig	11,200 (31%)
2400°F 16/1 P-ratio	1000°F/1500 psig	9750 (36%)
3000°F 16/1 P-ratio	1000°F/2400 psig	9000 (38%)

Higher combined-cycle thermal efficiencies will be obtained by employing more efficient coal gasification systems which have smaller associated heat losses. Using a low temperature purification system such as Benfield or Selexol, the best combined-cycle thermal efficiency exhibited by a moving bed gasifier will be from the one having the highest cold gas thermal efficiency, since in this case the irreversible sensible heat losses on gas cooling are minimized. A slagging gasifier has a high cold gas efficiency. Entrained bed gasifiers which do not make tars also tend to produce higher combined-cycle thermal efficiencies because the losses on cooling of the gas prior to purification are lower than in the moving bed case. This is because quenching, which is necessary when tars are produced, is not required.

Figure 9-2 shows the layout of a plant in which hydrogen sulfide is removed from the hot gasifier off-gas at, or near, gasifier exit temperature. This is not a demonstrated possibility but is being intensively studied at this time. Hot gas purification eliminates cooling irreversibilities and increases the combined-cycle thermal efficiency. It also increases the water consumption but may decrease pollution as no water treatment is required and no waste residues are produced.

The combined-cycle configuration provides the opportunity of desulfurizing a small volume of relatively high sulfur content fuel gas before its combustion, instead of scrubbing stack gas which has a low sulfur concentration. Processes for fuel gas H_2S scrubbing are more proven and developed than are processes for stack gas SO_2 scrubbing. The combination of improved thermal efficiency in clean fuel production and reasonable capital related costs are expected to make this method of power generation attractive.

9.4 DESIGN DETAILS OF GASIFIER AND COMBINED-CYCLE PLANTS

The following rules and procedure were used to design the plants for the purpose of determining the water streams. At the start a basis of 1000 lb of moisture-free coal was used. The coals are shown on Table 9-1. The gasifier rules used are:

(1) The ash contains 5 wt percent carbon.

(2) 11.08 percent of the carbon in the coal becomes carbon in CH_4.

(3) 1.37 percent of the carbon in the coal becomes carbon in C_2H_6.

(4) 11.3 wt percent of the moisture and ash-free coal is converted to naphtha, tar and oil having the composition shown on Table 9-6.

(5) 0.74 wt percent of the moisture and ash-free coal is converted to phenols having the composition shown on Table 9-6.

(6) The ratio of CO/CO_2 in the gas is 0.9 mole/mole. The carbon balance can now be completed.

(7) The ratio steam feed/oxygen in air is 3.77 mole/mole and 45 percent of the steam fed is decomposed. Moisture in the coal does not react. The oxygen balance can now be completed.

TABLE 9-6. GASIFIER MASS BALANCE USING WYOMING COAL

Basis: 1,000 lb dry coal

Material	Total (moles)	Total (lb)	C (moles)	H_2 (moles)	O_2 (moles)	N_2 (moles)	S (moles)	Ash (lb)
Coal		1302	56.37	41.67	14.03	0.36	0.25	74
Air; O_2	14.05				14.05			
N_2	52.86					52.86		
Steam	52.97			52.97	26.49			
TOTAL FEEDS			56.37	94.64	54.57	53.22	0.25	74
Gas; CH_4	6.25		6.25	12.49				
C_2H_6	0.39		0.77	1.16				
H_2	30.33			30.33				
CO	19.48		19.48		9.74			
CO_2	21.65		21.65		21.65			
H_2O	45.89			45.89	22.95			
H_2S	0.22			0.22			0.22	
N_2	52.86					52.86		
NH_3	0.63			0.95		0.32		
Naptha, Tar, Oil		104.64	7.47	3.37	0.19	0.04	0.03	
Phenols, etc.		6.85	0.43	0.22	0.04			
Ash; ash								74
C		3.89	0.32					
TOTAL PRODUCTS			56.37	94.63	54.57	53.22	0.25	74

(8) The hydrogen in the gas completes the hydrogen balance.

Table 9-6 gives a typical material balance for a gasifier. To complete the plant overall hydrogen balance and determine the process water streams, all that remains is to determine how much of the water in the gasifier product gas is condensed in gas clean-up. The gas leaving the sulfur removal system is taken to be saturated at 270 psia and 260°F and therefore to contain 13.1 vol percent water vapor. The sulfur removal system is taken to remove 5 percent of the CO_2 as well as the sulfur. These rules enable calculation of the hydrogen balance shown on Table 9-2 scaled to 1000 megawatts.

The next step is to check the gasifier heat balance. The rules used are:

(9) Gas leaves at 900°F and ash leaves at 500°F.

(10) 23 percent of the steam feed is raised in the jacket.

These rules result in a small loss, which is shown on Table 9-7 as point 4. Figure 9-3 shows a more detailed schematic than Figures 9-1 and 9-2 and is presented specifically to show points of heat input and output. These points are numbered and the results tabulated as Table 9-7. The calculations required to make Table 9-7 are as follows:

(11) Point 1, the coal input, is the basis.

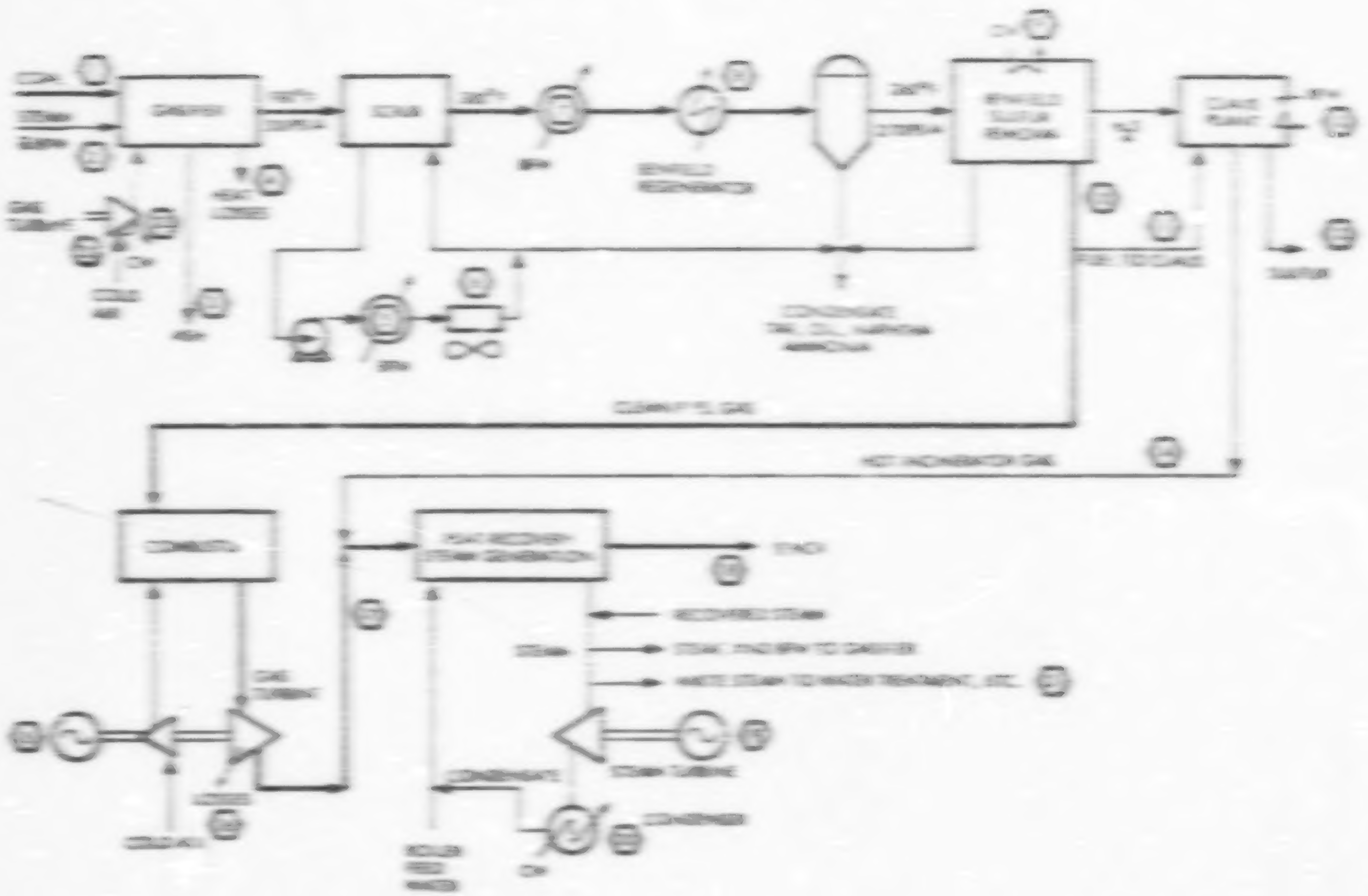
(12) Points 2, 3 and 4 come from the gasifier material and heat balances already described.

(13) Point 8, which is the heat needed in the Benfield regenerator, was supplied by the manufacturer. This system removes sulfur only, not carbon dioxide, and the rules given in Section 8 do not apply.

(14) Points 5, 6 and 7 are calculated from the temperatures given on Figure 9-3.

(15) In the Claus plant 95 percent of the H_2S is converted to sulfur. The residual gas is incinerated to convert it to SO_2. Calculations show that about 1 percent of the clean fuel is needed to raise the incinerated gas temperature to 1200°F. This fuel is not available to the gas turbine, but the hot gases are sent to heat recovery and the energy is mostly recovered. Points 12, 13 and 14 result from calculations on the Claus plant.

(16) To determine the energy at points 15, 16 and 17, the gas turbine-combustion-air compressor performance was simulated by using typical information. The simulation involves estimating an adiabatic efficiency for the



GASIFIER
CLEAN FUEL GAS
HOT INCINERATOR GAS
FUEL TO CLAUS
SULFUR
COMBUSTOR
STACK
RECOVERED STEAM
STEAM AND BFW TO GASIFIER
WASTE STEAM TO WATER TREATMENT, ETC.
GAS TURBINE
STEAM TURBINE
CONDENSATE
CONDENSER
BOILER FEED WATER

Figure 9-1. Generating plant details for heat balance.

TABLE 9.7. HEAT DUTIES AT THE VARIOUS POINTS IN THE PLANT SHOWN IN FIG. 9.3

Basis: 1000 lb dry coal
Units: 10^5 Btu

Point (see Fig. 9.3)		Wyoming	New Mexico	North Dakota
1.	Coal, HHV	11.95	11.66	11.27
2.	Steam + bfw to gasifier	1.02	1.01	0.94
3.	Ash	0.06	0.14	0.07
4.	Gasifier loss	0.42	0.54	0.19
5.	Scrubber recovery	1.11	0.56	1.12
6.	Scrubber air cooler	0.16	0.12	0.12
7.	Waste heat recovery	0.11	0.29	0.20
8.	Sulfur removal heat	0.11	0.11	0.12
9.	Sulfur removal cooling water	0.33	0.37	0.43
10.	Clean fuel	8.99	8.94	8.19
11.	Fuel to Claus incinerator	0.09	0.09	0.08
12.	Claus plant recovery	0.02	0.02	0.02
13.	Sulfur	0.03	0.03	0.03
14.	Claus incinerator gas	0.10	0.10	0.09
15.	Gas turbine generator	2.26	2.25	2.07
16.	Gas turbine losses	0.23	0.23	0.21
17.	Turbine exhaust gas	5.98	5.94	5.44
18.	Stack loss	2.10	2.05	1.90
19.	Steam turbine generator	1.14	1.07	1.09
20.	Steam turbine condenser	2.84	2.68	2.75
21.	Waste steam to water treatment and other uses	0.22	0.16	0.19
22.	Air compressors	0.43	0.43	0.39
23.	Gasifier air compressor interstage cooling	0.08	0.08	0.08

turbine and air compressor, and a cooling air flow. The temperature of the combustion products is held to 1950°F.

(17) To calculate point 18, the stack temperature is taken to be 300°F.

(18) Plant steam balances were made to complete the calculation. The steam turbine generator efficiency of 28.4 to 28.6 percent represents a combination of high pressure and low pressure turbines.

Table 9-8 is presented as a check on Table 9-7. Table 9-9 shows the electricity produced so that the designs can be scaled to 1000 megawatts to make the summary Tables 9-2 and 9-3. In these plants tar, oil and naphtha are not burnt but are sold. The actual station efficiencies are 26 to 28.5 percent. The efficiencies of 33.4 to 33.7 percent are presented for illustration only. If the tar, etc., were to be burnt on site, the water requirements would alter.

9.5 EFFECT OF HOT GAS DESULFURIZATION

Hot gas desulfurization has been discussed in Section 8.1. The use of such a process will increase the station efficiency by an amount dependent on the gasifier and the available gas turbine. This is shown on Table 9-10. The Higas process yields a much hotter gas than the Lurgi process and the advantage of hot gas desulfurization is significant. If hot gas desulfurization is used, condensate will not be recovered. This will increase the water requirement, but because tars, etc., will pass straight to the combustor, the cost will be reduced and pollution problems may be lowered.

9.6 COOLING IN A POWER PLANT

To convert "wet cooling load" (in Btu/hr) to water evaporated in the cooling tower (in lb water/hr), we must determine the cooling rate in the tower (in Btu dissipated/lb water evaporated). This is not the same in electric generating plants as in fuel-to-fuel conversion plants (Hygas, Synthane and Solvent Refined Coal). This is because the turbine characteristics for conversion plants are those of industrial turbines, not the larger drives used in generating plants. In the fuel-to-fuel conversion plants the

TABLE 9-3. PLANT ENERGY BALANCES

Units: 10^6 Btu/1000 lb dry coal

Point (see Fig. 9-3)		Wyoming	New Mexico	North Dakota
10 - 11	Fuel to gas turbine	8.90	8.85	8.11
15	Gas turbine generator	2.26	2.25	2.07
16 + 22	Gas turbine loss and air compressor drives	0.60	0.66	0.60
17	Turbine exhaust gas	5.98	5.94	5.44
	Subtotal-gas turbine outputs	8.90	8.85	8.11
14 + 17 - 18	Heat from gas given to steam generation	3.98	3.99	3.63
5 + 7 + 12	Waste heat recovered	1.24	0.87	1.34
	Subtotal-steam produced	5.22	4.86	4.97
19	Steam turbine generator	1.14	1.05	1.09
20	Steam turbine condenser	2.84	2.64	2.75
2	Gasifier steam	1.02	1.01	0.94
21	Waste steam used	0.22	0.16	0.19
	Subtotal-steam used	5.22	4.86	4.97
1	Coal	11.95	11.66	11.27
15 + 19	Electricity	3.40	3.32	3.16
-	Fuel value of tar, oil, naptha, phenol, ammonia, sulfur	1.97	1.85	1.98
-	Sensible heat of recovered fuel and condensate	0.17	0.12	0.22
4 + 6 + 16 + 18	Gasifier losses, dry cooling, gas turbine loss and stack loss	2.87	2.94	2.42
9 + 20 + 23	Cooling water	3.25	3.13	3.26
3	Ash	0.06	0.14	0.07
21	Waste steam used	0.22	0.16	0.19
	Total energy outputs	11.94	11.66	11.30

TABLE 9-9. PLANT EFFICIENCIES

Basis: 1000 lb dry coal

	Wyoming		New Mexico		North Dakota	
	10^6 Btu	kw-hr	10^6 Btu	kw-hr	10^6 Btu	kw-hr
Coal	11.95		11.66		11.27	
Electricity	3.40	996	3.32	973	3.16	926
Naphtha, tar and oil, heat value	1.84	184[a]	1.67	167[a]	1.83	183[a]
Other products, heat value	0.13		0.18		0.15	
Unrecovered heat	6.58		6.49		6.13	
Station efficiency for electricity	28.5%		28.5%		28.0%	
Station efficiency including use of tar to generate electricity	33.7%		33.4%		33.6%	

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[a] Assuming 10,000 Btu/kw-hr with the tar burned in a boiler to raise steam.

TABLE 9-10. EFFICIENCIES OF VARIOUS PLANT COMBINATIONS (FROM REFERENCE 4, TABLE 45)

Gasifier	Sulfur Removal	Gas Turbine	Station Efficiency
Bu Mines Stirred Bed	Selexol	First generation	31.4%
"	Iron Oxide (hot gas)	"	33%
Bigas	Selexol	"	31.9%
"	Consol (hot gas)	"	37.6%
"	Selexol	Second generation	36%
"	Consol (hot gas)	"	42.3%

cooling towers are bypassed in winter months to prevent too low a temperature in the condenser. Bypassing is not practiced in generating plants. Furthermore, the decision as to whether to use wet or dry cooling in the turbine condensers is economic and is made differently in the fuel-to-fuel plants from the generating plants, because a somewhat different set of costs is taken into account.[5-8]

In calculating water requirements for the combined cycle power plants, the following conditions have been used:

	Cooling rate in tower (Btu/lb water evaporated)	Turbine condenser cooling method
Wyoming	1,401	wet/dry; 25% of all wet
New Mexico	1,357	all wet
North Dakota	1,484	all wet

These results come from a separate study in which cooling in coal fired steam-electric power plants was investigated. The turbines in these plants are not quite the same as the steam turbines in combined-cycle plants (the steam pressure is different), but the water consumption will be close. (The computations were made by R.W. Beck and Associates for subcontracted work done by Water Purification Associates for the University of Oklahoma under Subcontract No. 1916-1, Prime Contract EPA 68-01-1916.) The optimized conditions for an evaporative cooling system and for two dry cooling systems (one using the same turbine as in the wet system and the other using a probable design of a future high back pressure turbine) are shown on Table 9-11. The annual cooling costs are shown on Table 9-12. On Table 9-13 the results are summarized. Dry cooling will be used if water supply and treatment costs are more than the breakeven costs used. If wet cooling is used, the quantity of water evaporated (averaged over the year) can be calculated from the cooling load and the cooling rate in the tower shown on the table.

In the same study a partial analysis of combined wet/dry cooling in New Mexico was made. The result is shown on Figure 9-4. A very recent report[9] points out that even if wet condensing is apparently more economical the added cost of dry condensing can be small. In Braintree, Massachusetts (on

TABLE 9-11. SUMMARY OF DESIGN CONDITIONS FOR OPTIMIZED COOLING SYSTEMS FOR COAL FIRED GENERATING PLANTS (10^6 KW)

	Dry Cooling High Back Pressure Turbine		
	Beulah, N. Dakota	Gillette, Wyoming	Farmington, New Mexico
Average Annual Dry-Bulb Temperature, °F	42	46	51
Average Annual Wet-Bulb Temperature, °F			
Design Wet-Bulb Temperature, °F			
Ambient Temperature for Determination of Peaking Capacity Requirement, °F	82.0	82.0	82.0
Initial Temperature Difference, °F	39	34	31
Design Cooling Range, °F	14.50	15.0	17.5
Design Approach Temperature, °F			
Design Terminal Temperature Difference, °F	5.0	7.0	6.0
Design Inlet Temperature, °F	81.6	79.1	79.6
Turbine Exhaust Pressure, in Hga	2.0	2.0	2.0
Total Tower Heat Load, 10^6 Btu/hr	4647.0	4647.0	4647.0
Condenser Duty, 10^6 Btu/hr	4587.0	4567.0	4587.0
Circulating Water Flow, 10^3 gpm	634.9	611.6	593.9
Condenser			
Surface Area, 10^3 sq.ft.	622	512	551
Number of Tubes, 10^3	91	81	43
Tube length, ft	26	28	49
Velocity through tubes, ft/sec.	6.98	6.94	6.95

(Continued)

TABLE 9-11 (continued)

	Dry Cooling High Back Pressure Turbine		
	Beulah, N. Dakota	Gillette, Wyoming	Farmington, New Mexico
Average Annual Dry-Bulb Temperature, °F	42	46	51
Average Annual Wet-Bulb Temperature, °F			
Design Wet-Bulb Temperature, °F			
Ambient Temperature for Determination of Peaking Capacity Requirement, °F	82.0	82.0	82.0
Initial Temperature Difference, °F	68.0	67.0	68.0
Design Cooling Range, °F	34.0	33.5	34.0
Design Approach Temperature, °F			
Design Terminal Temperature Difference, °F	5.0	5.0	5.0
Design Inlet Temperature, °F	81.0	82.1	85.0
Turbine Exhaust Pressure, in Hga	3.5	3.5	3.8
Total Tower Heat Load, 10^6 Btu/hr	5211	5211	5212
Condenser Duty, 10^6 Btu/hr	5144	5144	5146
Circulating Water Flow, 10^3 gpm	304.2	308.7	304.6
Condenser			
Surface Area, 10^3 sq.ft.	451	462	452
Number of Tubes, 10^3	44	46	45
Tube length, ft	39	38	38
Velocity through tubes, ft/sec.	6.92	6.68	6.73

(continued)

TABLE 9-11 (continued)

	Evaporative Cooling		
	Beulah, N. Dakota	Gillette, Wyoming	Farmington New Mexico
Average Annual Dry-Bulb Temperature, °F	42	46	51
Average Annual Wet-Bulb Temperature, °F	36	37	40
Design Wet-Bulb Temperature, °F	71	69	64
Ambient Temperature for Determination of Peaking Capacity Requirement, °F			
Initial Temperature Difference, °F			
Design Cooling Range, °F	27.43	24.55	26.53
Design Approach Temperature, °F	20.0	20.0	28.0
Design Terminal Temperature Difference, °F	7.0	7.0	7.0
Design Inlet Temperature, °F	91.0	89.0	92.0
Turbine Exhaust Pressure, in Hga	4.0	3.5	4.0
Total Tower Heat Load, 10^6 Btu/hr	4722	4694	4722
Condenser Duty, 10^6 Btu/hr	4661	4634	4661
Circulating Water Flow, 10^3 gpm	344.3	382.3	357.3
Condenser			
Surface Area, 10^3 sq.ft.	427	457	438
Number of Tubes, 10^3	49	56	52
Tube length, ft	33	33	32
Velocity through tubes, ft/sec	6.94	5.75	6.81

TABLE 9-12. SUMMARY OF ANNUAL EVALUATED COSTS FOR OPTIMIZED COOLING SYSTEMS (10^6 DOLLARS/YR FOR 1000 MEGAWATTS, 6125 STEAM-HR/YR)

	Beulah, N. Dakota	Gillette, Wyoming	Farmington, New Mexico
Dry Cooling, Conventional Turbine			
Annual capital, & operation & maintenance cost of cooling system	10.786	10.069	10.555
Annual plant fuel cost	27.411	27.414	27.413
Credit for excess generation	-0.343	-0.325	-0.317
Annual replacement capacity & energy cost	0.834	0.834	0.803
Annual auxiliary power & energy cost	2.847	2.284	2.750
Total annual evaluated cost	41.535	40.285	41.204
Dry Cooling, High Back Pressure Turbine			
Annual capital, & operation & maintenance cost of cooling system	6.707	6.060	6.054
Annual plant fuel cost	29.361	29.362	29.360
Credit for excess generation	-0.431	-0.436	-0.401
Annual replacement capacity & energy cost	1.263	0.801	1.143
Annual auxiliary power & energy cost	1.554	1.593	1.613
Total annual evaluated cost	38.454	37.380	37.770
Evaporative Cooling			
Annual capital, & operation & maintenance cost of cooling system	2.272	2.233	2.062
Annual plant fuel cost	27.407	27.414	27.406
Credit for excess generation	-0.162	-0.177	-0.070
Annual replacement capacity & energy cost	0.406	0.057	0.490
Annual auxiliary power & energy cost	0.595	0.615	0.569
Total annual evaluated cost	30.518	30.142	30.457

TABLE 9-11. SUMMARY OF COMPARISON OF WET AND DRY COOLING IN COAL FIRED GENERATING PLANTS (10^3 MW)

	Beulah, N. Dakota	Gillette, Wyoming	Farmington, New Mexico
Water evaporated in wet cooling (gallons per stream-hr)	381,780	402,180	417,780
Breakeven cost of water ($/1000 gallons)			
Conventional turbine	4.71	4.12	4.19
High back-pressure turbine	2.96	2.94	2.85
Tower heat load (10^6 Btu/stream-hr)	4,722	4,694	4,722
Cooling rate in tower Btu/lb water evaporated	1,484	1,401	1,357

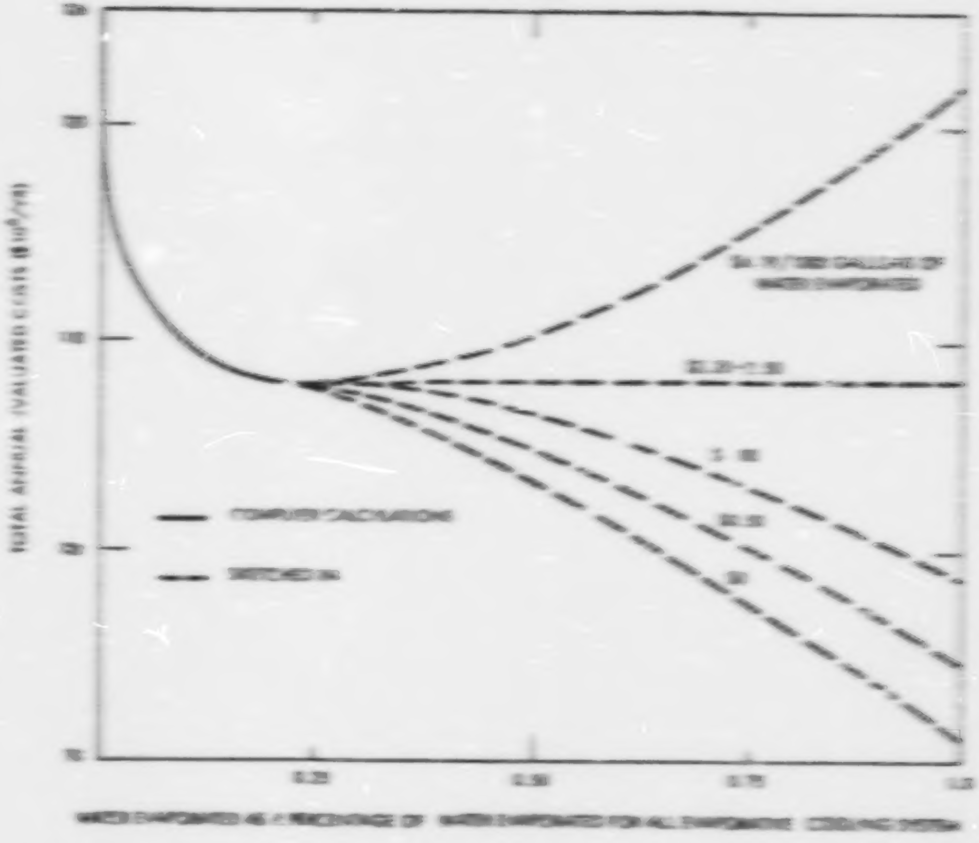

Figure 3-4. Total annual evaluated costs of wet/dry cooling system as a percentage of evaporative loss of all evaporative cooling in New Mexico.

the coast south of Boston) an 85 MW combined-cycle generating plant is planned (65 MW gas turbine and 20 MW steam turbine). Suitable water costs $0.70/thousand gallons, and dry cooling has been chosen.

In tabulating water quantities in Section 13, all wet condenser cooling was assumed in North Dakota and New Mexico; and in Wyoming, because of the high cost of water and for illustration, combined wet/dry cooling was assumed with the water consumption being one quarter of the water required for all wet cooling.

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SECTION 10

COOLING

10.1 INTRODUCTION

All fuel conversion plants are less than 100 percent efficient. The higher heating value of the product fuel plus the heating value of combustible byproducts and wastes is less than the heating value of the coal taken in. Since the first law of thermodynamics is obeyed, that part of the energy in the coal which is not recovered as fuel must be lost to the atmosphere in some way. A major part of each of the plant designs made in this study is the determination of the ultimate disposition of unrecovered heat. In each of the design sections, the ultimate disposition of unrecovered heat is tabulated. Some of the unrecovered heat leaves the plant as hot flue gas up a chimney, water vapor from drying coal, convective and radiant losses from electric motors and container surfaces and similar ways, all called direct losses. Direct losses are those for which cooling water cannot be used.

The remaining unrecovered heat leaves through a heat transfer surface. In this study two types of heat transfer equipment are considered: 1) finned tube heat exchangers with fans for forced air cooling or dry cooling or air cooling; and 2) shell and tube heat exchangers using circulating cooling water, itself cooled in a mechanical draft evaporative cooling tower, called wet cooling or evaporative cooling. For all the major points of cooling using heat transfer surfaces, a decision must be made on how much water will be evaporated to dispose of the unwanted heat. The study is economic, and there are four factors to be accounted for in choosing a cooling system:

(i) The capital cost difference must be determined. In general, dry coolers cost more than wet coolers for a given heat removal, and the cost difference increases when the heat is removed at lower temperature levels. The additional capital cost of dry cooling must also include the greater installed cost of all plant compressors on which dry cooling is used.

(2) The energy needed to operate the cooling system must be determined; this is the energy needed to operate fans and to circulate cooling water.

(3) In some circumstances, notably steam turbine condensers, the plant operation consumes more energy if the temperature of cooling is raised. This fuel penalty must be determined.

(4) Finally, the cost of water for evaporative cooling must be considered. This is discussed below.

These various cost factors will be discussed at each of the following important points of cooling in the plants:

cooling process streams
cooling the acid gas removal regenerator condenser
condensers for steam turbines
interstage cooling in gas compressors.

The designs have usually incorporated air cooling to about 140°F and wet cooling below this.

Cooling Process Streams

The conclusion of the study on cooling process streams is that air cooling should be used to about 140°F and wet cooling below this. This result has already been incorporated into the previous design section.

Cooling the Acid Gas Removal Regenerant Condenser

Because in the area of the country under study water is scarce and expensive, dry coolers have been used in all acid gas removal systems. This is discussed below. This is quite common practice in chemical plants and refineries and is incorporated into many coal conversion plant designs.

Condensers for Steam Turbines

The cooling of steam turbine condensers is a very large part of the total plant cooling load and is complicated to study. This load is discussed in several sections below, and great emphasis is placed on combined dry and wet cooling. The choice of cooling varies from site to site. All wet cooling was selected in North Dakota and wet/dry cooling at the other sites.

Interstage Cooling in Gas Compressors

Cooling between stages of gas compression is also complicated to study. This load is discussed in Section 10.9 below, and it turns out that wet cooling is preferred at New Mexico and wet/dry cooling at Wyoming. At North Dakota we have assumed wet cooling as at New Mexico.

10.2 THE COST OF WATER

Water is not free. In most Western states water must be bought from its source. A modest cost of water rights is in the range of $10 to $20 per acre-foot, which is 3¢ to 5¢ per thousand gallons. The cost of moving water to the sites of interest in this study is about 1.2¢/(thousand gallons)(mile).[1] Finally, circulating cooling water must be treated, and the minimum cost is 20¢/thousand gallons evaporated. For comparing two plants a raw water cost of 40¢/thousand gallons has been recommended.[2] This might be the cost of water rights plus transportation from 30 miles or uphill pumping from a lake or underground. When treatment is added, cooling water can often cost 60¢/thousand gallons evaporated. This is probably the low end of the cost. As distance from the water to the plant increases to 100 miles or more, or as the cost of water rights increases, and when water is more contaminated necessitating more expensive treatment, the cost of water evaporated for cooling can approach $2/thousand gallons evaporated. In this study we have considered the effect of the cost of cooling water in the range $0.60 to $2/thousand gallons evaporated.

10.3 COOLING PROCESS STREAMS

Below 270 to 300°F, useful heat cannot be extracted from a process stream and further cooling must dissipate the heat to the atmosphere. A simple calculation shows it is probably best to cool to about 130 to 140°F using an air cooler and to cool below this temperature using a wet system. The economics prove to be a trade-off between the cost of water and the cost of money. An example is now given:

A methane stream at 1,000 psig is to be cooled from 280 to T°F. The ambient air temperature is 90°F. Cooling water is available at 80°F and may be heated to 105°F. The heat removed in the cooling tower may be assumed to be 1,400 Btu/lb of water evaporated (see Section 10.4 for a discussion of this number which depends on the climate). The conditions of the process stream are such that the heat transfer coefficient for dry cooling is 70 Btu/(hr)(ft^2)(°F) and for wet cooling is 100 Btu/(hr)(ft^2)(°F). The data used for this and other calculations on cooling is given on Table 10-1.

First, we find the cost of removing 10^6 Btu/hr by dry cooling using, as our example, a cooled temperature T = 130°F. The air temperature rise (see Table 10-1) is

$$\Delta t = (0.005)(70)\left(\frac{280 + T}{2} - 90\right) = 40.25 \quad \text{(where T = 130°F)}$$

The high temperature difference, $\Delta_1 = 280 - (90{+}t) = 149.75$ (where T = 130°F).

The low temperature difference $\Delta_2 = T - 90 = 40$ (when T = 130°F).

The log mean temperature difference = $(\Delta_1 - \Delta_2)/\ln(\Delta_1/\Delta_2) = 83.1$.

The heat exchanger area $A = Q/(\text{LMTD})(U) = 10^6/(83.1)(70) = 172\ \text{ft}^2$.

The charges for the heat exchangers are \$18/ft^2 × 0.17/yr × A ft^2 = \$526/yr = \$0.0658/hr for 8,000 hrs/yr.

The cost of running the fan is

$$(0.0175A \times 0.7455,\ \text{kw}) \times (2¢/\text{kw-hr}) = \$0.0449/\text{hr}$$

Total cost \$0.11/hr or \$0.11/10^6 Btu.

TABLE 10-1. REPRESENTATIVE FORMULAE AND DATA USED FOR CALCULATING COST OF WET AND DRY COOLING

1. Heat Transfer Coefficients (U)

		U, Btu/(hr)(ft^2)($^\circ$F)*	
		Dry	Wet
Condensing steam from turbine drives		130	400
Condensing steam in presence of noncondensible gases in gas purification regenerator		75	110
Cooling methane at 1,000 psig		70	100
Cooling water for off-gas scrubbing		120	170
Air and oxygen compressor interstage coolers:	psig		
	10	10	12
	50	20	20
	100	30	40
	300	40	50
	≥500	50	70

---

*Based on bare tube area of finned tubes for dry coolers.

2. Heat Transfer Area

(a) Dry Cooling:

The following empirical formula for air temperature rise was used

$$\Delta t = 0.005\ U\left[\frac{T_1 + T_2}{2} - t_1\right]$$

Here, t_1 is the inlet air temperature and T_1, T_2 are the process stream inlet and outlet temperatures. This formula is suitable for estimating purposes. In actual designs the rise must be optimized. The other formulae for calculating the heat transfer area are standard.

(b) Wet Cooling:

The rise in water temperature has usually been assumed to be 25°F. In actual designs this may be controlled by the limitation set on the maximum turbine back pressure, here taken to be 5 in. Hg. absolute. In most cooling systems the water chemistry, particularly scaling tendencies, also controls the permitted temperature rise. Standard heat transfer formulae were used to calculate areas.

(continued)

TABLE 10-1 (continued)

3. Energy for Cooling

Dry cooler fans: Horsepower = 0.015 x Area ($U < 50$)
= 0.0175 x Area ($50 \leq U < 100$)
= 0.02 x Area ($U \geq 100$)

Cooling tower fans: Horsepower = 0.013 x gpm circulated

Cooling water circulation pumps: Horsepower = 0.033 x gpm circulated

4. Costs

	Cost	Pressure (p,psig)	Annual Charges for Amortization Plus Maintenance
Heat Exchangers*:			
Dry cooling	$\$10/ft^2$**	--	17%/yr
Wet cooling	$\$5.1/ft^2$	$p < 300$	20%/yr
	$\$5.6/ft^2$	$300 \leq p < 450$	
	$\$6.1/ft^2$	$450 \leq p < 600$	
	$\$8.9/ft^2$	$p \geq 600$	
Other:			
Cooling tower	$7/gpm circulated		15%/yr
Electrical energy	2¢/kw-hr		
Steam	$\$1.80/10^6$ Btu		

---

*Installed but without piping, valving, instrumentation, engineering or other costs. These costs are for comparison of wet and dry cooling only, not for absolute plant costs. The energy and cost figures are typical, but variations are to be expected for actual design.

**Based on bare tube area of finned tubes.

Now we find the cost of removing 10^6 Btu/hr by wet cooling. When $T = 130°$, the log mean temperature difference =

$$\frac{(280 - 105) - (130 - 80)}{\ln \frac{280 - 105}{130 - 80}} = 100°F$$

The heat transfer area = $10^6/(100)(100) = 100\ ft^2$

The charges for the heat exchangers are

$$\$8.9/ft^2 \times 0.2/yr \times A\ ft^2 = \$178/yr = \$0.0223/hr$$

The circulation rate is

$$10^6\ Btu/hr \times 1\ lb/25\ Btu = 40{,}000\ lb/hr = 80\ gal/min$$

The cooling tower charges are

$$\$7/gpm \times 80\ gpm \times 0.15/yr = \$84/yr = \$0.0105/hr$$

Operating the tower fan plus circulating pump costs

$$0.045\ hp/gpm \times 80\ gpm \times 0.7455\ kw/hp \times 2¢/kw\text{-}hr = \$0.0537/hr$$

For free water the total cost is \$0.0865/hr = \$0.0865/10^6 Btu.

The rate of evaporation of water is

$$10^6\ Btu/hr \times 1\ lb/1{,}400\ Btu = 714\ lb/hr = 0.0857 \times 10^3\ gal/hr$$

This calculation and others are plotted on Figure 10-1. On Figure 10-2, entitled "Cost of Cooling a Low Pressure Gas Stream," the calculations have been repeated for the case:

U, dry cooling = 40 Btu/(hr)(ft^2)(°F)
U, wet cooling = 50 Btu/(hr)(ft^2)(°F)
cost of wet area = \$5.6/ft^2

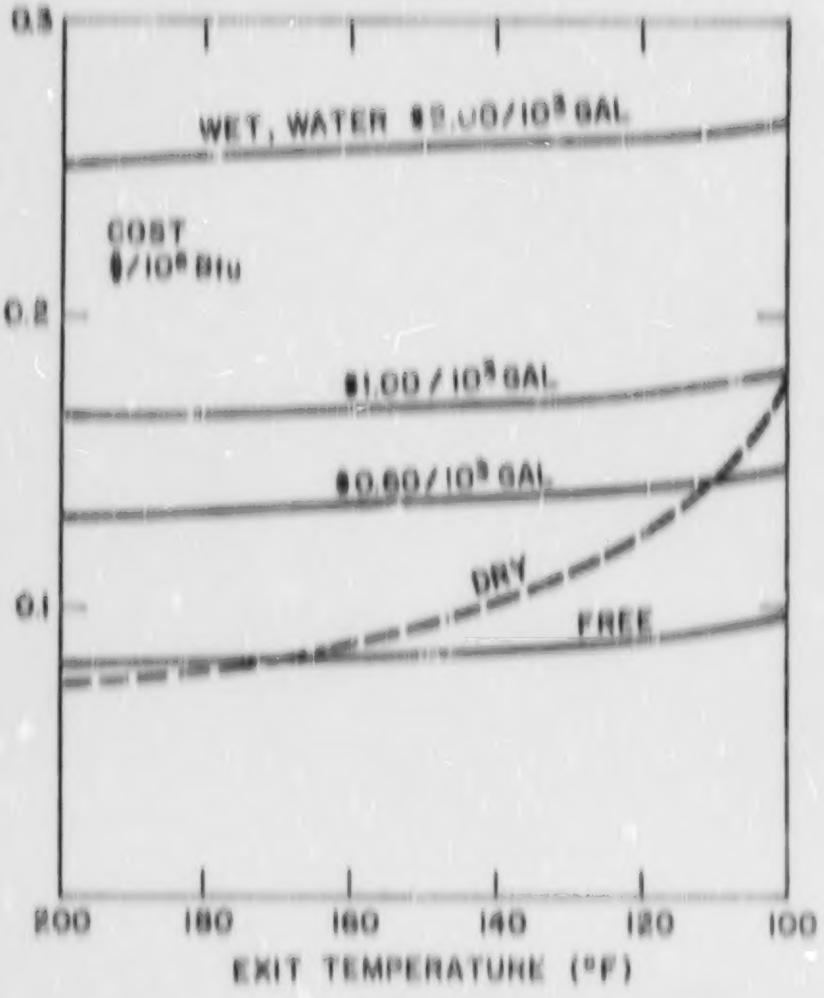


Figure 10-1. Cost of cooling a high pressure methane stream.

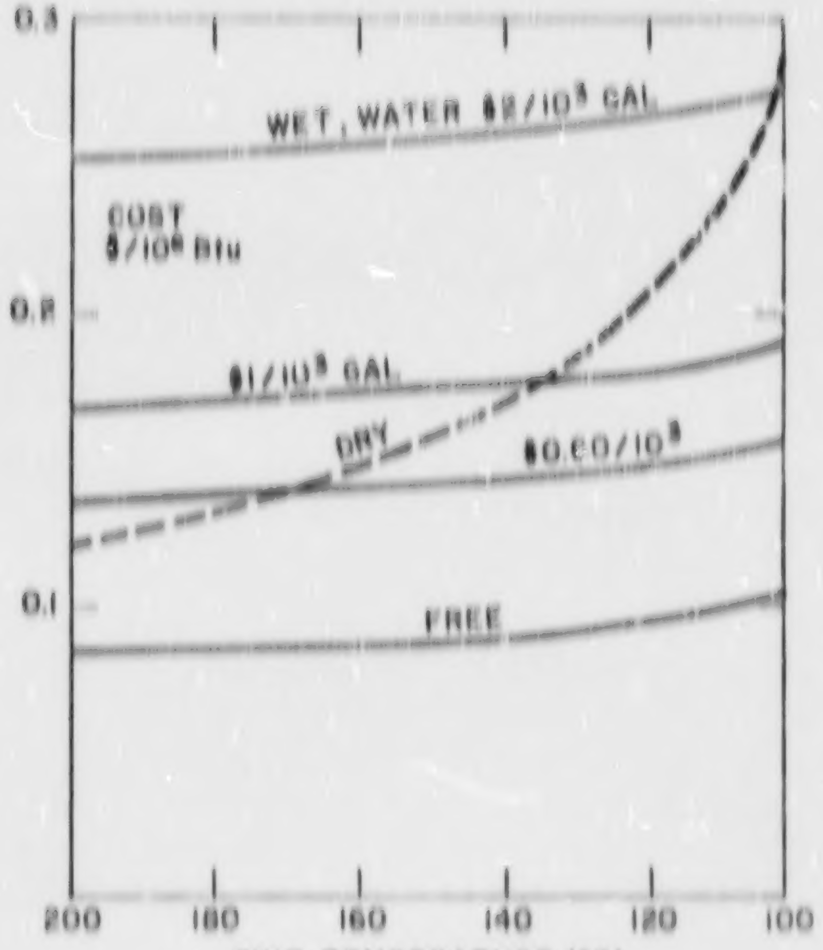


Figure 10-2. Cost of cooling a low pressure gas stream.

It is clear that the choice of wet or dry cooling depends on all the process conditions as well as the cost of water and should be made for each situation individually. As an adequate estimate, process streams have been cooled to 140°F using dry cooling and below this using wet cooling.

10.4 WATER EVAPORATED FOR WET COOLING

Given that a certain cooling load in Btu/hr is to be lost through wet cooling, it is necessary to know how much water must be evaporated in the cooling tower to remove this load.

In a wet or evaporative cooling tower as shown in Figure 10-3, the warm water leaving the heat exchanger is pumped to the top of the tower where it is distributed through an assembly of nozzles. It then passes through the heat transfer zone and is collected in the basin. The splash packing, or fill material, inside the tower retards and breaks up the water into fine droplets creating both a large droplet surface area and high residence time. Since heat is removed from the water droplets through evaporation and convection, the larger the surface area of the droplets, the higher is the heat transfer efficiency. Air is circulated through the tower, either by natural convection (natural draft tower) or by a mechanical fan (mechanical draft tower), to remove the evaporated water and sensible heat from the tower. Makeup water is required to replace the evaporated water, and the drift and blowdown are required to eliminate the accumulation of solids in the circulating water.

The evaporation rate of the tower to remove a certain heat load depends on the design of the tower, the relative flow rates of water and air, the entering warm water temperature, the temperature and humidity of the entering air and the annual average evaporation rate. Btu/lb water evaporated depends on how the tower is operated, that is, on whether the tower is bypassed and what cold water temperature is maintained. For the purpose of this study the cooling tower is operated to give the best performance when coupled with all wet cooling of steam turbine condensers as described in Sections 10.7 and 10.8. As an example, Table 10-4 gives the heat removal rate (Btu/hr) and the water consumption rate (lb/hr) for such an all wet

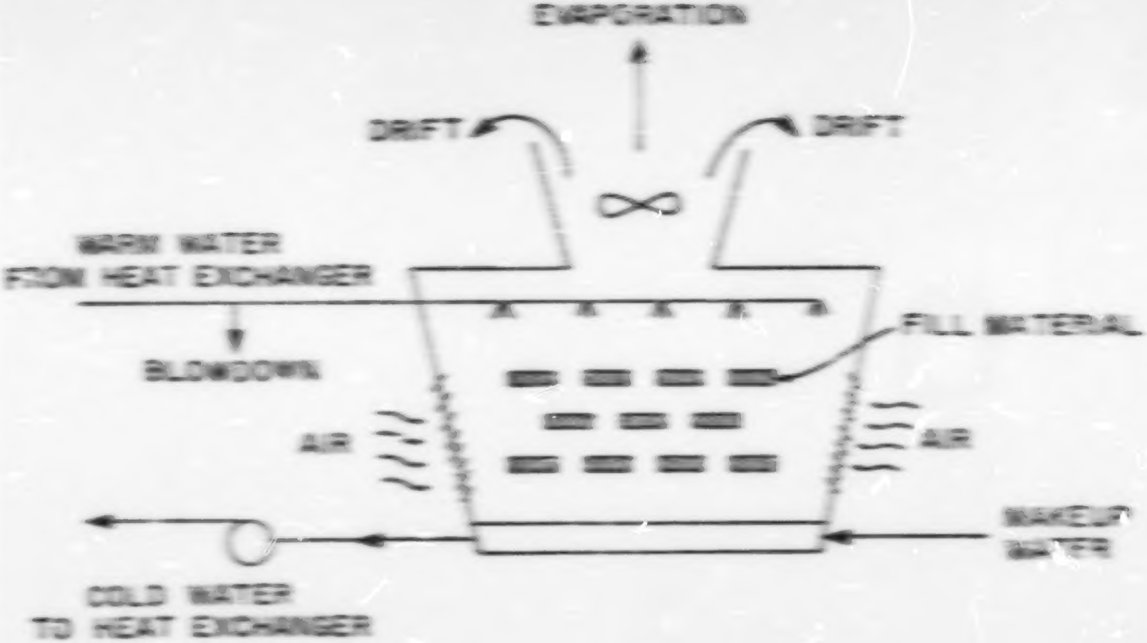

EVAPORATION
DRIFT
DRIFT
WARM WATER
FROM HEAT EXCHANGER
BLOWDOWN
FILL MATERIAL
AIR
AIR
MAKEUP
WATER
COLD WATER
TO HEAT EXCHANGER

Figure 10-1. Schematic of wet cooling tower.

system in Casper, Wyoming. The monthly averages are:

Month	Btu/lb Water Evaporated
1, January	1475
2, February	1472
3, March	1438
4, April	1440
5, May	1345
6, June	1308
7, July	1272
8, August	1300
9, September	1328
10, October	1399
11, November	1487
12, December	1493

The annual average is 1397 Btu/lb water evaporated. This number, and the other numbers given on Table 10-2, will be used to estimate the water consumed for wet cooling of process streams in Section 11. (As explained in Section 9.6, Table 10-2 is not used for power generation.)

10.5 COOLING IN ACID GAS REMOVAL

Removal of the acid gases, carbon dioxide and hydrogen sulfide, is an important energy-consuming part of the coal conversion plants and the regenerator condenser is a large cooling load. (For power generation, carbon dioxide is not removed and this discussion does not apply.) In the process designs two acid gas removal systems have been considered: a Benfield hot potassium carbonate type and a Selexol physical solvent type. In each case

TABLE 10-2. ANNUAL AVERAGE WATER CONSUMPTION FOR WET COOLING

	Btu/lb Water Evaporated
Wyoming	1397
North Dakota	1420
New Mexico	1375

the feed stream to the condenser is a mixture of water vapor and noncondensible carbon dioxide at about 230°F. For condensing steam in the presence of the noncondensible gas, the recommended heat transfer coefficients are 75 Btu/(hr)(ft^2)(°F) when dry condensing and 110 Btu/(hr)(ft^2)(°F) when wet condensing.[1] Condensation proceeds as the vapor mixture is cooled. For a Benfield type system, cooling to 140°F will condense enough water to keep the circulating absorbent in balance.

Calculating by the method used for cooling process streams, the cost for Benfield type condensers is \$0.116/10^6 Btu when air cooling and the same cost when wet condensing if water costs 46¢/thousand gallons. Dry condensing is assumed for this study.

For a Selexol type process it is probably necessary to cool to 100°F to keep the water in the system in balance. By air cooling to 130°F and then wet cooling to 100°F, 90 percent of the total cooling load is taken by the air cooler and 10 percent by the wet cooler. (The feed stream contains about 1.4 moles H_2O/mole CO_2. The stream saturated at 130°F contains about 0.18 moles H_2O/mole CO_2 and the stream saturated at 100°F contains about 0.07 moles H_2O/mole CO_2.)

10.6 CHARACTERISTICS OF STEAM TURBINES

Since the cooling load on steam turbine condensers is a large part of the plant cooling load, it is necessary to conduct detailed studies to determine the relative amounts of wet or dry cooling to be employed. Examples of various types of cooling are discussed in the following two sections. The numerical results depend on the characteristics of the turbine.

In a steam turbine drive system the steam rate required by the turbine to produce a certain shaft power output depends on the inlet steam condition, the condenser pressure and the turbine efficiency. Usually the higher the inlet steam pressure and temperature, the higher will be the thermal efficiency of the system. In the present application where the steam is partially produced by waste heat recovery, the usual steam pressure is in the range from 715 to 915 psia, and the superheated temperature in the range from 600° to 900°F. Also, in the present application where the steam turbine drive is used mainly for gas compression purposes, the type of turbine drive used usually has a maximum efficiency of about 80 percent when the condenser pressure is in the range of 3 to 5 in Hg absolute. The corresponding steam saturation temperatures for the two condenser pressures are 115 and 134°F, respectively. Above 134°F or below 115°F, efficiency falls.

The heat rates required when the condenser temperature is in the range of 115 to 134°F have been calculated for the various inlet steam conditions mentioned and are plotted in Figure 10-4. The calculations were made using a turbine efficiency of 80 percent and a bearing efficiency of 95 percent. The results in Figure 10-4 show that the steam rates for the four inlet steam conditions are quite close and that they can be represented by a single straight line going from a steam rate value of 11,700 Btu/kw-hr at the condenser temperature of 115°F to a value of 13,200 Btu/kw-hr at the condenser temperature of 134°F.

The increase in steam rate with condenser temperature indicates that there is a certain fuel penalty to be considered in evaluating the cost of various cooling systems.

The condenser cooling loads when the condenser temperature is in the range of 115 to 134°F have also been calculated for the four inlet steam conditions mentioned and are plotted in Figure 10-5. The results indicate that the condenser loads for the four inlet steam conditions are also quite close and that they can be represented by a single straight line, going from a value of 8,200 Btu/kw-hr at the condenser temperature of 115°F to a value of 8,700 Btu/kw-hr at the condenser temperature of 134°F. This typical line will be used for condenser load calculations when the economics of condenser cooling systems are evaluated.

10.7 DRY AND WET COOLING SYSTEMS FOR TURBINE CONDENSERS

For a turbine condenser cooling system direct dry cooling, wet cooling or a combination of both have been considered. The cost and the water consumption rate of each has been analysed for the climates of Beulah, North Dakota, Casper, Wyoming and Farmington, New Mexico. The details of the all dry system, the all wet system and the wet/dry combination will be discussed. The results of month-by-month calculations for the three sites and the

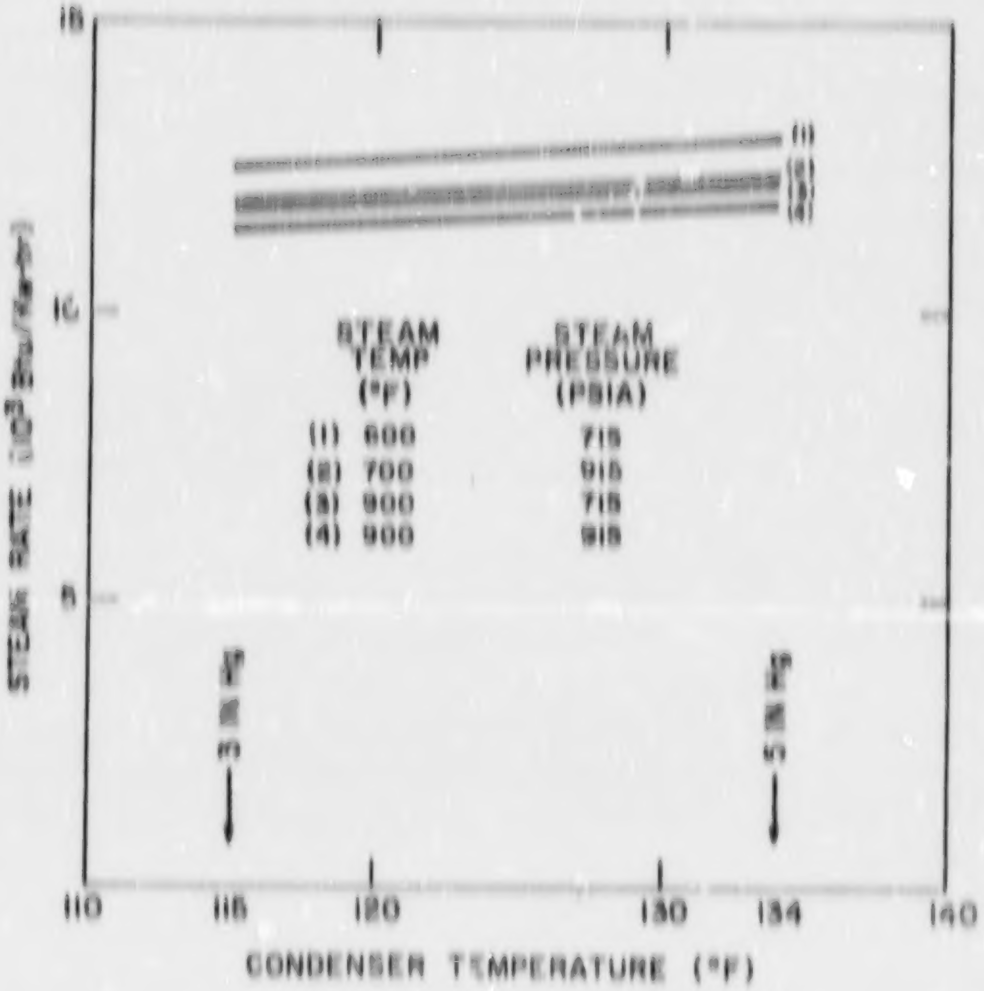


Figure 10-4. Turbine heat rates.

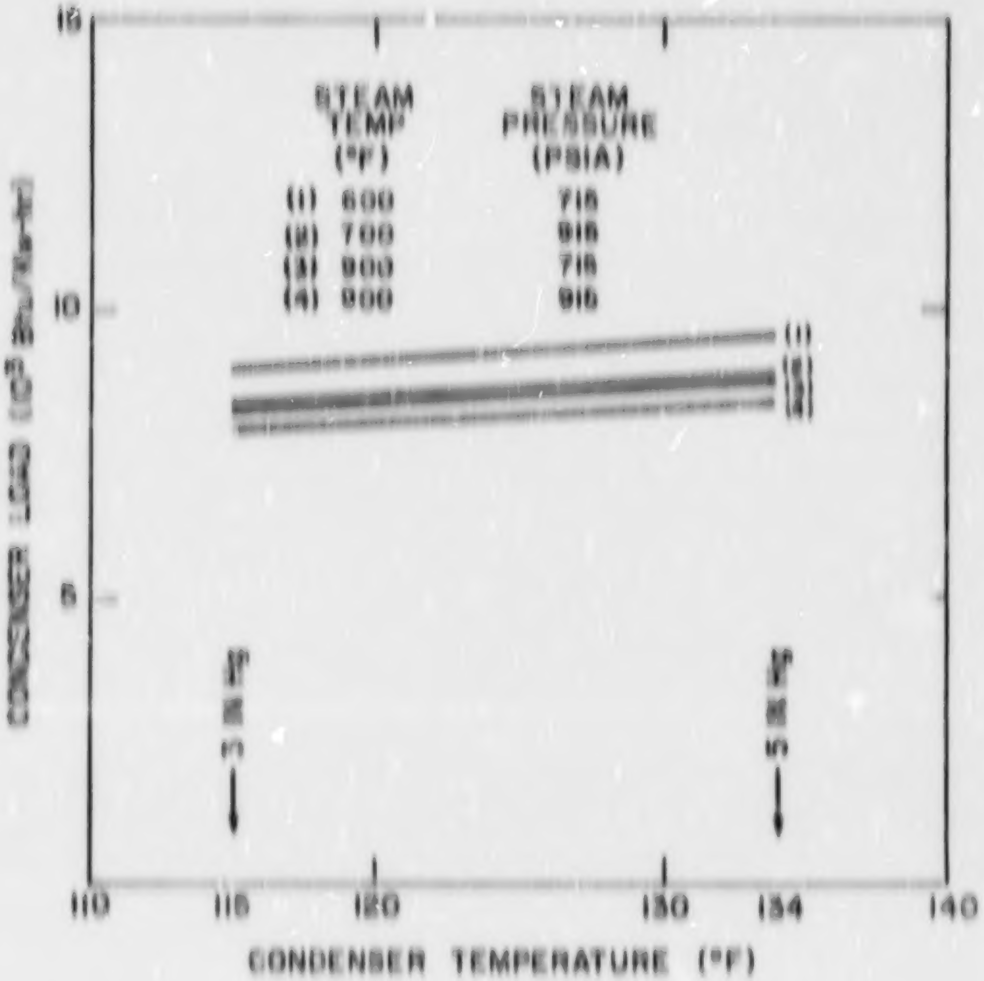


Figure 10-5. Turbine condenser cooling loads.

analysis of the results will be presented in the next section.

In the all dry system the condenser is assumed to be cooled directly by air (see Figure 10-6 assuming that the wet cooling section is not present) and is assumed to be held within the temperature range of 115 to 134°F. The condenser is designed to have a maximum temperature of 134°F when the ambient air is at the summer design temperature. As the ambient temperature drops during the year, the condenser temperature also drops eventually reaching 115°F. If the ambient temperature drops further the power to the fans, which are of the variable speed or variable pitch type, is reduced. The reduction of the fan power reduces the air flow rate through the condenser and, thus, the heat transfer rate so that the condenser temperature can be maintained at 115°F.

The heat transfer rate in a condensing heat exchanger is given by the equation

$$Q_{OD} = UA_D\left(\frac{(T_C - T_{AC}) - (T_C - T_{AH})}{\ln \dfrac{T_C - T_{AC}}{T_C - T_{AH}}}\right) \qquad (1)$$

where Q_{OD} is the heat transfer rate (Btu/hr) for the dry condenser, U is the heat transfer coefficient (Btu/(hr)(ft^2)(°F)), A_D is the dry condenser surface area (ft^2), T_C is the condenser temperature (°F), T_{AC} and T_{AH} are the inlet cold air temperature (°F) and the exit warm air temperature (°F) respectively. The air temperature rise $(T_{AH} - T_{AC})$ is given by the empirical equation (see Table 10-1)

$$(T_{AH} - T_{AC}) = 0.005\, U(T_C - T_{AC}) \qquad (2)$$

Finally, from Section 10.6, the condenser load is a function of condenser temperature T_C

$$Q_{OD} = 8,200 + 500\left(\frac{T_C - 115}{134 - 115}\right) = 5,174 + 26.3\, T_C \qquad (3)$$

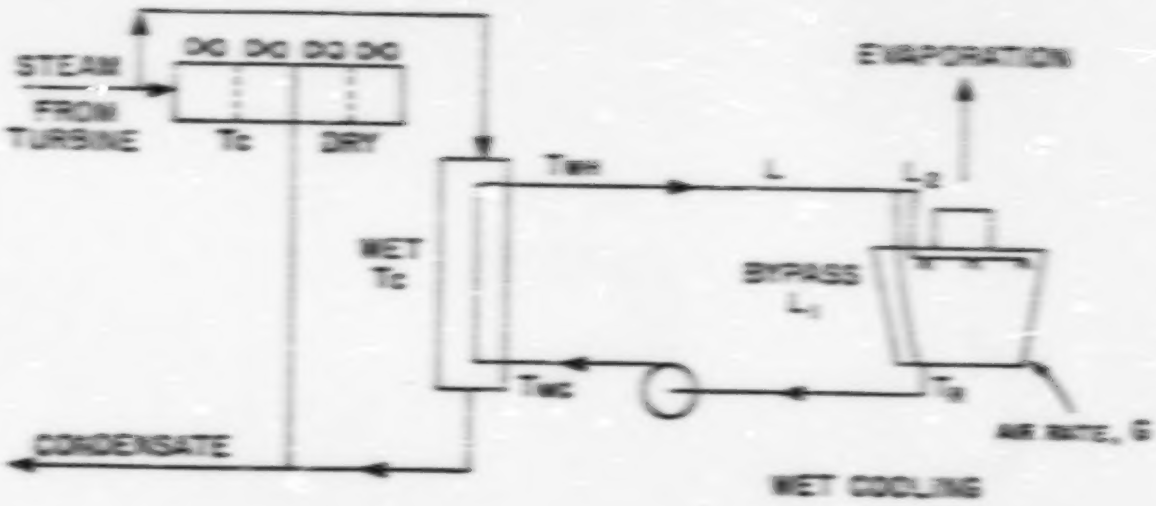

STEAM
FROM
TURBINE
Tc
DRY
WET
Tc
TWH
L
L2
EVAPORATION
BYPASS
L1
TWC
TA
AIR RATE, G
CONDENSATE
WET COOLING

Figure 10-6. Turbine condenser cooling systems.

For a given design temperature T_{AC}, which in this study is close to peak summer temperature (see following tables), these relationships make it possible to calculate the condenser area A_D. To find A_D, T_C is taken as 134°F, U is taken to be 130 Btu/(hr)(ft^2)(°F) for all air condenser calculations. For any other nondesign, ambient air temperature, it is then possible to calculate the condenser temperature T_C by trial and error. When T_C comes out to be less than 115°F, it is taken to be 115°F and the fan power is reduced. The reduction in fan power to maintain the condenser temperature at 115°F is a function of the ambient temperature drop below that temperature when the condenser is at 115°F. The relationship used is a typical example shown on Figure 10-7. Actual variations in fan power and in the high and low condensing temperature will depend on the type of equipment selected.

In the all wet system the condenser is cooled by circulating water which evaporates in the wet cooling tower (see Figure 10-6 assuming the dry cooling portion is not present). The cooling water is assumed to be circulated through the condenser at a constant rate. The wet tower has, however, multiple cells operating at the same water-to-air flow ratio. The condenser is assumed to operate in the temperature range of 115 to 134°F. At the summer design condition the condenser is designed to have a temperature of 134°F. As the ambient temperature drops during the year, the condenser cools eventually to a temperature of 115°F. If the ambient temperature continues to drop in the colder months of the year, the multiple cells in the wet tower are shut off one by one. Each cell is shut off by turning the fan off so the water passes to the basin without any cooling. This allows the returning cooling water to the condenser to be such as to maintain the condenser temperature at 115°F during these colder months (below 115°F, turbine efficiency falls). Shutting off of parts of the cooling tower has the benefit of saving fan energy.

The heat transfer rate in the wet condenser is given by the equation

$$Q_{CW} = UA_W \left(\frac{(T_C - T_{WC}) - (T_C - T_{WH})}{\ln \dfrac{T_C - T_{WC}}{T_C - T_{WH}}} \right) \qquad (4)$$

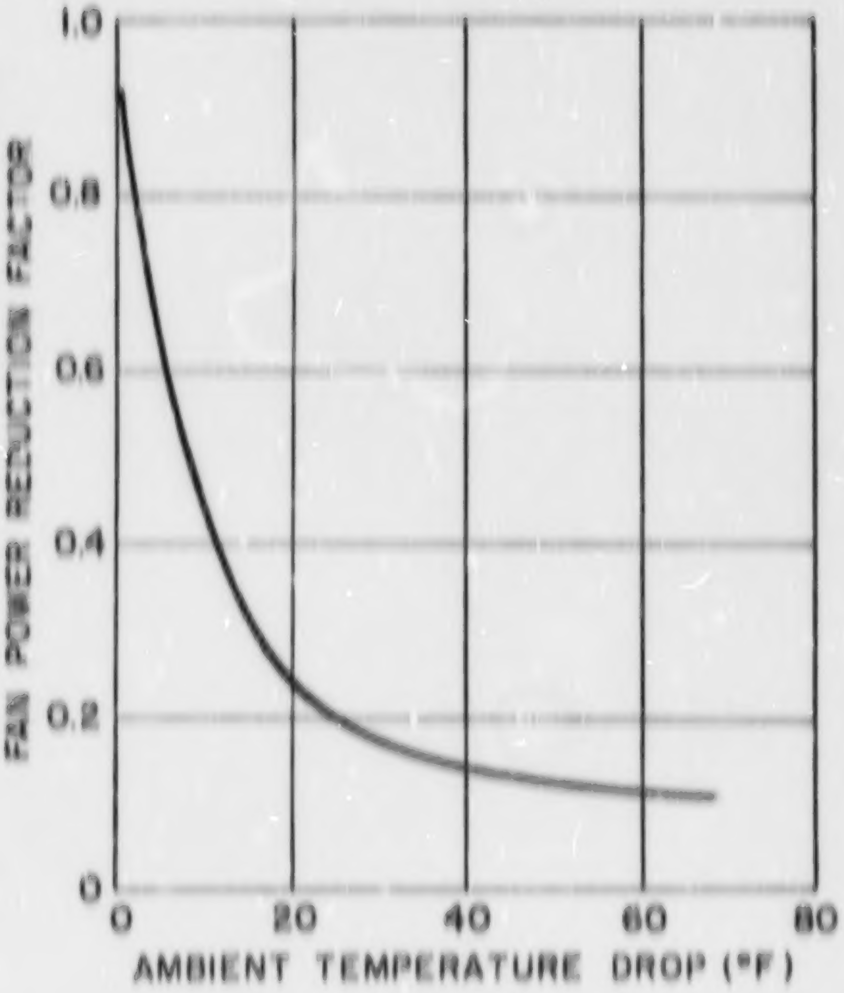


Figure 10-7. Fan power reduction factor for air coolers.

where Q_{CW} is the heat transfer rate (Btu/hr) for the wet condenser, U is the heat transfer coefficient, Btu/(hr)(ft^2)(°F), A_W is the wet condenser surface area (ft^2), and T_{WC} and T_{WH} are the inlet and exit cooling water temperatures respectively. The heat transfer coefficient U has been taken as 400 Btu/(hr)(ft^2)(°F).

The rate of heat removal by the circulating water is

$$Q_{CW} = C\,L(T_{WH} - T_{WC}) \tag{5}$$

where C is the heat capacity of water, 1 Btu/(lb)(°F), and L is the cooling water circulation rate (lb/hr).

Equations (4) and (5) for a wet condenser are similar to equations (1) and (2) for a dry condenser. From section 10.6, the condenser load Q_{CW}, Btu/shaft kw, is known as a function of condenser temperature T_C. The relationship is Equation (3). For summer design temperatures we have chosen T_{WC} (cold water temperature) = 99°F, T_{WH} (hot water temperature) = 124°F and the condenser temperature T_C = 134°F. This enables the calculation of the water circulation rate L, and wet condenser area A_W. For a chosen summer design wet bulb temperature, the cooling tower can also be designed. The cooling tower was designed using Reference 4. (The procedure is described in Reference 4 and other texts on cooling tower design. Fill type H, 30 ft fill height, 18 ft air travel were used with the wet bulb temperature suitable for the site, 99°F cold water temperature and 25°F range; this fixes the tower characteristic KaV/L and the water-to-air ratio L/G.)

When the ambient wet bulb temperature falls below design, the cold water temperature, the condenser temperature and the hot water temperature fall. Given an off-design wet bulb temperature, a trial-and-error calculation is used to find the water and condenser temperatures for the design condenser and the design cooling tower. Equations (4) and (5) are used along with the cooling tower curves from Reference 4.

When the ambient wet bulb is such that the condenser would fall below 115°F, some cooling tower fans are shut off to hold the condenser at 115°F. The bypass is shown in Figure 10-6. The bypass rate L_1 is given by

$$T_{WC} = T_{WH} - \left(\frac{L - L_1}{L}\right) (T_{WH} - T_B) \qquad (6)$$

The final part of a wet condenser calculation is to determine the rate of evaporation of water. The cooling load, which was transferred from the steam to the circulating water in the condenser, is transferred from the circulating water to the air in the cooling tower. Thus the enthalpy of air is increased by a known amount as it passes through the tower. This increase in enthalpy shows up as an increase in humidity plus, usually, an increase in temperature. The enthalpy of the air entering the tower is known from climatic data and so the enthalpy of air leaving the tower can be calculated. If now the relative humidity of the air leaving the tower is known, the humidity can be determined. The relative humidity of air leaving a countercurrent tower can readily be calculated.[5] However, an error of not more than 4 percent is made by taking the relative humidity of exit air to be 100 percent (whether cross- or counter-flow). The rate of evaporation of water is the air flow rate through the tower, G, multiplied by the difference in humidity between the top and bottom of the cooling tower.

In the wet/dry combination the system is designed so that at the summer design peak load condition the cooling load is divided in predetermined proportions between a dry and a wet condenser (Figure 10-6). At the design point the condenser temperature is at 134°F with all the fans in the dry condenser and all the units in the wet tower operational. Also, the inlet and exit cooling water temperatures in the wet tower, without any bypass, are 99 and 134°F, respectively. As the ambient temperature drops during the year, both dry and wet towers are allowed to operate at full power. The condenser temperature drops eventually to 115°F when the ambient temperature is cold enough. If the ambient temperature continues to drop, the units in the wet tower are gradually shut off (the dry section is still operating at full power) so that the condenser temperature remains at 115°F. This shifts the condensing load from the wet tower to the dry condenser and reduces the amount of water evaporated in the wet tower. As the ambient temperature continues to drop during the year, more wet units are shut off until eventually the wet tower is completely shut down. All the cooling load is now in the dry condenser. If the ambient temperature continues to drop further, fan power in the dry condenser is reduced to maintain the condenser temperature at 115°F.

The benefits of the wet/dry combination are that the capital investment is less than that of an all dry system and the water consumption rate is less than that of an all wet system. In the following section the operating cost and the water consumption rate for different combinations of wet and dry systems will be evaluated for the three sites considered. The wet/dry system chosen for this study should be considered as illustrative only. Other steam and water flow arrangements should be studied when evaluating a particular site. Discussions concerning alternative arrangements may be found in References 6 and 7.

10.8 WATER CONSUMPTION FOR TURBINE CONDENSERS AT SPECIFIC SITES

As an example, consider the climatic conditions of Casper, Wyoming. Table 10-3 shows the results of month-by-month calculations for an all dry condenser. The condenser area is first found for the summer design condition: ambient air $T_{AC} = 96°F$; condenser temperature $T_C = 134°F$; load $Q_{OD} =$ 8,700 Btu/kw-hr. From Equation (2)

$$T_{AH} - T_{AC} = T_{AH} - 96 = 0.005\, U(T_C - T_{AC}) = (0.005)(130)(38) = 24.7$$

so

$$T_{AH} = 120.7$$

From Equation (1)

$$Q_{OD} = 8{,}700 = UA_D \left(\frac{T_{AH} - T_{AC}}{\ln \dfrac{T_C - T_{AC}}{T_C - T_{AH}}} \right)$$

TABLE 10-1. WATER CONSUMPTION RATE PER SHAFT KW FOR AN ALL DRY SYSTEM AT CASPER, WYOMING

MONTH	1	2	3	4	5	6	7	8	9	10	11	12
DBT (°F)	24	26	32	41	54	65	71	70	59	47	32	30
WBT (°F)	20	22	27	34	44	51	55	53	46	38	27	25
Q_{WS} (Btu/hr)	0	0	0	0	0	0	0	0	0	0	0	0
T_{WC} (°F)	—	—	—	—	—	—	—	—	—	—	—	—
T_{WE} (°F)	—	—	—	—	—	—	—	—	—	—	—	—
T_R (°F)	—	—	—	—	—	—	—	—	—	—	—	—
WET FAN POWER (10^{-3} Kw)	0	0	0	0	0	0	0	0	0	0	0	0
PUMP POWER (10^{-3} Kw)	0	0	0	0	0	0	0	0	0	0	0	0
WATER CONSUMPTION (lb/hr)	0	0	0	0	0	0	0	0	0	0	0	0
Q_{DS} (Btu/hr)	8200	8200	8200	8200	8200	8200	8200	8200	8200	8200	8200	8200
DRY FAN POWER (10^{-3} Kw)	5.10	5.10	5.53	5.95	8.28	14.0	21.2	19.6	10.2	6.80	5.53	5.53
T_C	115	115	115	115	115	115	115	115	115	115	115	115
FUEL PENALTY	0	0	0	0	0	0	0	0	0	0	0	0

DESIGN DBT = 96°F
DESIGN WBT = 60°F

WET CONDENSER AREA = 0
DRY CONDENSER AREA = 1.65 ft^2
WET CIRCULATION RATE = 0

so

$$A_D = 2.85 \text{ ft}^2$$

The installed fan power = 0.02 A_D hp = 0.0425 kw.

Now consider month 7, which is the hottest month of the year. The monthly average dry bulb temperature T_{AC} = 71°F. The calculation is trial-and-error. For a first try assume T_C = 115°F so that, from Equation (3), Q_{OD} should be 8,200. From Equations (2) and (1) we calculate Q_{OD} to be 11,000. In fact, Q_{OD} = 8,200 when the ambient air temperature T_{AC} = 79°F. Since the monthly average temperature is 8°F below 79°F, the monthly average fan power is (from Figure 10-7) 0.5 × 0.0425 = 0.0212 kw. The other monthly calculations involve only a calculation of fan power.

Table 10-4 shows the results for an all wet system. The summer design conditions are Q_{OW} = 8,700, T_C = 134°F, T_{WC} = 99°F, and T_{WH} = 124°F. From Equation (5) the water circulation rate L = 348 lb/hr = 0.696 gal/min. From Equation (4) the condenser area A_W = 1.09 ft^2. The cooling tower design is taken from Reference 4, and the following is assumed for an example: the fill characteristic curve for cross-flow fill type H, 30 ft high with 18 ft of air travel, crosses the tower operating curve for 60°F wet bulb temperature (the design wet bulb), 25°F range and 39°F approach when KaY/L = 1.1 and L/G = 2.8. At this point the two curves are simultaneously satisfied, and this fixes the cooling tower. Finally, from Table 10-1, the water circulation pump requires 0.033 × gpm,hp = 0.0171 kw and the installed tower fan power = 0.012 × gpm,hp = 0.0061 kw.

Now consider again month 7, the hottest month of the year; the monthly average dry bulb temperature T_{AC} is 71°F and the wet bulb temperature WBT is 55°F. The calculation is trial-and-error. If the cold water temperature to the condenser is assumed to be 98°F, the warm water leaving the condenser, based on Equations (4) and (5) in Section 10-7, is 123°F and the condenser temperature is 133°F with a cooling load of 8,680 Btu/hr. Now with the ambient wet bulb temperature at 55°F and the cooling tower characteristics fixed at KaY/L = 1.1 and L/G = 2.8, the cooling water leaving the tower would have a temperature of 98°F, the same as the initially assumed temperature. No bypass is necessary in this month. Also, given L/G = 2.8 in the

TABLE 10-4. WATER CONSUMPTION RATE FOR [illegible] FOR AN ALL WET SYSTEM AT CASPER, WYOMING

MONTH	1	2	3	4	5	6	7	8	9	10	11	12
DBT (°F)	26	28	32	41	54	65	71	70	59	47	32	30
WBT (°F)	20	22	27	34	44	51	55	53	46	38	27	23
Q_{SR} (Btu/hr)	8330	8330	8225	9410	8597	8644	8680	8680	8619	8462	8225	8330
T_{WC} (°F)	87	82	83	89	94	97	99	99	96	71	82	82
T_{WH} (°F)	106	106	106	113	119	122	123	123	121	115	106	106
T_S (°F)	77	78	83	89	94	97	98	98	96	71	82	82
WET TOWER POWER (10^{-3} kWe)	5.83	5.33	6.10	6.27	6.10	6.10	6.10	6.10	6.10	6.10	6.10	6.10
PUMP POWER (10^{-3} kWe)	17.1	17.1	17.1	17.1	17.1	17.1	17.1	17.1	17.1	17.1	17.1	17.1
WATER CONSUMPTION (lb/hr)	5.36	5.57	5.72	5.86	6.39	6.61	6.86	6.88	6.64	6.25	5.53	5.47
Q_{DR} (Btu/hr)	0	0	0	0	0	0	0	0	0	0	0	0
DRY TOWER POWER (10^{-3} kWe)	0	0	0	0	0	0	0	0	0	0	0	0
T_C (°F)	117	115	116	123	130	132	133	133	131	125	116	115
FUEL PENALTY (Btu/hr)	0	0	0	8.45	15.9	20.4	21.2	20.8	17.9	10.3	0	0

DESIGN DBT = 96°F
DESIGN WBT = 68°F

WET CONDENSER AREA = 1.23 ft^2
DRY CONDENSER AREA = 0
WET CIRCULATION RATE = 0.286 GPM

tower and L = 348 lb/(hr)(kw), the air flow rate through the tower can be calculated as 124 lb/(hr)(kw), and the enthalpy of the air is increased by a value of 70 Btu/lb. Assuming the air coming out from the tower is completely saturated, the change in humidity of the air is 0.055 lb H_2O/lb air; the evaporation rate therefore is 6.84 lb/hr.

The same calculation procedure can be repeated for the other months, except for months 1 and 2, and the results are shown in Table 10-4 indicating a gradual drop in condenser temperature and a gradual reduction in fuel penalty. For months 1 and 2, the calculation procedure can be repeated except that bypass is required in order to keep the condenser temperature at 115°F. For example, in month 1 the cold and hot water temperatures of the condenser are 82 and 106°F respectively in order to keep the condenser at 115°F. With a wet bulb temperature of 20°F, the temperature of the cooling water leaving the tower is 77°F. A bypass of the tower, therefore, is necessary in order to maintain the temperature of the return cooling water at 82°F.

Table 10-5 shows the results for a typical wet/dry combination. This is a "50%" example, because the dry area is half the all-dry area, the wet area is half the all-wet area, and the water circulation rate is half the all-wet rate. The system is run with full fan power and no bypass for months 7 and 8. For four more months--5, 6, 9 and 10--the cooling tower is partly bypassed. For the rest of the year the cooling tower is not used, and the fan energy to the dry condenser is reduced.

From the month-by-month calculations the annual average figures were taken for various wet/dry combinations and recorded on Table 10-6 as annual consumption figures assuming 7,008 hrs/yr. The annual cost is given on Table 10-7. Unit costs are given on Table 10-1. The annual cost from Table 10-7 is plotted in Figure 10-8 as a function of water consumption for different water costs, from free-of-charge to $\$2/10^3$ gallons. Also shown in Figure 10-8 is the percentage of wet cooling at peak summer design condition, which is a measure of the relative wet tower size. Figure 10-8 shows that for a water cost of less than $\$0.68/10^3$ gallons, it is more economical to have an all wet system, whereas for a water cost of more than $\$0.68/10^3$ gallons and up to a value of $\$2/10^3$ gallons it is more economical to have a wet/dry

TABLE 10-5 WATER CONSUMPTION [illegible]

MONTH	1	2	3	4	5	6	7	8	9	10	11	12
DBT (°F)	26	26	32	41	54	65	71	70	59	47	32	30
WBT (°F)	20	22	27	36	46	51	55	53	46	39	27	25
Q_{W} (Btu/hr)	0	0	0	0	1217	2411	2757	2997	1788	418	0	0
T_{WC} (°F)	—	—	—	—	109	95	91	91	101	112	—	—
T_{WB} (°F)	—	—	—	—	112	109	108	108	111	114	—	—
T_{D} (°F)	—	—	—	—	91	91	91	91	95	98	—	—
WET FAN POWER (10^{-3} kW)	0	0	0	0	1.14	2.36	3.06	3.06	1.45	0.30	0	0
PUMP POWER (10^{-3} kW)	0	0	0	0	0.56	0.56	0.56	0.56	0.56	0.56	0	0
WATER CONSUMPTION (lb/hr)	0	0	0	0	0.88	1.87	2.28	2.29	1.18	0.31	0	0
Q_{DS} (Btu/hr)	[illegible]	[illegible]	[illegible]	[illegible]	6083	5725	5263	5263	6422	7782	[illegible]	[illegible]
DRY FAN POWER (10^{-3} kW)	5.36	5.96	8.40	17.4	21.2	21.2	21.2	21.2	21.2	21.2	8.46	7.50
T_{C} (°F)	125	125	125	125	125	125	125	125	125	125	125	125
[illegible] (Btu/hr)	0	0	0	0	0	0	0	0	0	0	0	0

DESIGN DBT = 95°F

DESIGN WBT = [illegible]°F

WET CONDENSER AREA = [illegible] ft²

DRY CONDENSER AREA = 1.42 ft²

WET CIRCULATION RATE = [illegible]

TABLE 10-6. EQUIPMENT SIZE AND ANNUAL POWER REQUIREMENT PER SHAFT KW FOR TURBINE CONDENSER COOLING AT CASPER, WYOMING

WET LOAD FRACTION	0%	25%	50%	75%	100%
DRY AREA (ft^2)	2.85	2.13	1.42	0.711	0
DRY FAN POWER (kw-hr/yr)	65.5	89.6	105	74.3	0
WET AREA (ft^2)	0	0.272	0.544	0.816	1.09
COOLING TOWER SIZE (GPM)	0	0.174	0.348	0.522	0.696
PUMP POWER (kw-hr/yr)	0	6.91	30.0	89.7	120
WET FAN POWER (kw-hr/yr)	0	0.766	6.60	21.1	41.7
FUEL PENALTY (10^6Btu/yr)	0	0	0	0.016	0.068
WATER CONSUMPTION (gal/yr)	0	70.7	627	2580	5100

ANNUAL OPERATING HOURS = 7008

TABLE 10-7. ANNUAL OPERATING COST (\$/(shaft kw)(yr)) FOR TURBINE CONDENSER COOLING AT CASPER, WYOMING

WET LOAD FRACTION	0%	25%	50%	75%	100%
DRY AREA	8.72	6.52	4.35	2.18	0
DRY FAN POWER	1.31	1.79	2.10	1.49	0
WET AREA	0	0.28	0.55	0.83	1.11
COOLING TOWER	0	0.18	0.37	0.55	0.73
PUMP POWER	0	0.10	0.60	1.79	2.40
WET FAN POWER	0	0.01	0.13	0.42	0.8[illegible]
FUEL PENALTY	0	0	0	0.03	0.[illegible]
TOTAL COST IF WATER COST FREE	10.0	8.88	8.10	7.29	5.1[illegible]
TOTAL COST IF WATER COST IS \$1/10^3 GAL	10.0	8.95	8.73	9.87	10.[illegible]
TOTAL COST IF WATER COST IS \$2/10^3 GAL	10.0	10.0	9.35	12.5	15.[illegible]

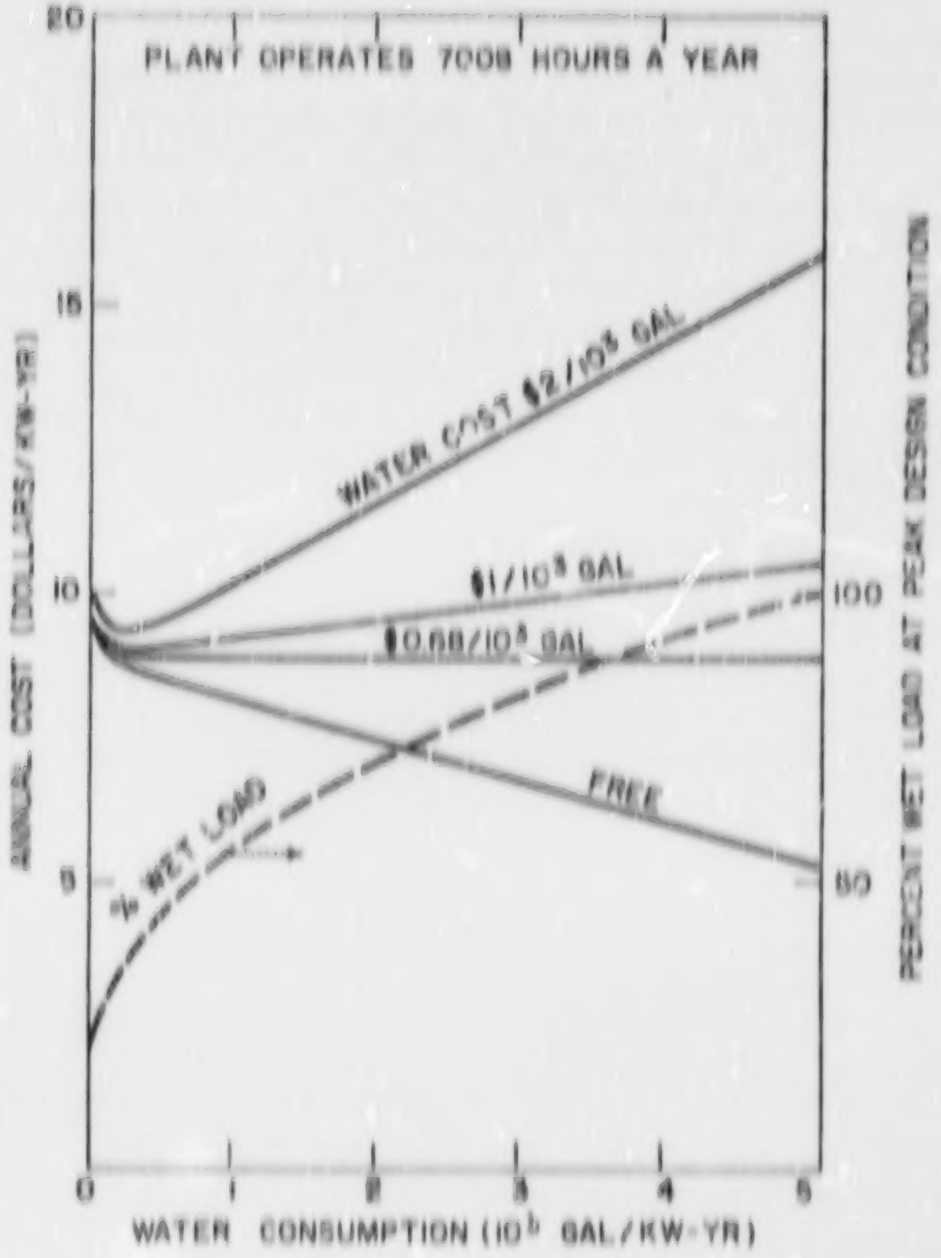


Figure 10-8. Annual cost of steam turbine condenser cooling at Casper, Wyoming.

combination. Based on this economic consideration, the water consumption rate for various water costs can be obtained and are shown in Figure 10-11. Figure 10-11 shows that if the water cost for Casper, Wyoming is more than \$0.65/10^3 gallons, a wet/dry cooling combination is justified and the volume of water consumed is reduced by a factor of 10. The month-by-month calculations and the annual operating costs and water consumption rates shown in Tables 10-3 to 10-7 have been repeated for the climates of Beulah, North Dakota and Farmington, New Mexico. The month-by-month and peak design temperatures for those two locations are listed in Table 10-8. Figures 10-9 and 10-10 show results of the calculation with the annual operating cost as a function of the water consumption rate for various water costs. The optimal annual water consumption rates for various water costs are determined from these two figures and are shown in Figure 10-11. Figure 10-11 shows that if the water cost is more than \$0.78/10^3 gallons and \$0.66/10^3 gallons for Farmington and Beulah, respectively, wet/dry cooling combination should be used for the two locations and the annual water consumption rate can be reduced by a factor of 10.

Figures 10-8 to 10-10 also show that the all wet system and the all dry system would cost the same if the water cost is \$0.90/10^3 gallons for Casper, Wyoming, \$1.05/10^3 gallons for Farmington, New Mexico and \$1.10/10^3 gallons for Beulah, North Dakota.

10.9 WATER CONSUMPTION FOR INTERSTAGE COOLING ON GAS COMPRESSION

The remaining major point of cooling is interstage cooling on gas compressors. Each compressor requires a separate study. All that has been done for this project is to study a three-stage air compressor designed to pump air from the ambient temperature and 15 psia to 95°F and 90 psia, in which condition the air enters the separation plant to be separated into oxygen and nitrogen. Air compressors for this service are the largest compressors in SNG plants and any conclusions reached about interstage cooling can safely be applied also to the oxygen compressors.

Figure 10-12 shows the assumed design conditions for dry, wet and dry/wet. Trim wet cooling is required in the dry section because the compressed

TABLE 10-8. MONTHLY AVERAGE TEMPERATURE OF BEULAH, NORTH DAKOTA AND FARMINGTON, NEW MEXICO

	FARMINGTON, N.M.		BEULAH, N.D.	
Month	DBT(^{o}F)	WBT(^{o}F)	DBT(^{o}F)	WBT(^{o}F)
1	26	23	8	7
2	33	28	15	13
3	42	33	26	21
4	49	37	43	37
5	60	45	56	47
6	70	51	65	57
7	76	58	72	62
8	73	57	70	60
9	64	49	58	50
10	51	41	46	39
11	39	32	28	25
12	27	24	18	17
DESIGN PEAK	98	65	102	71

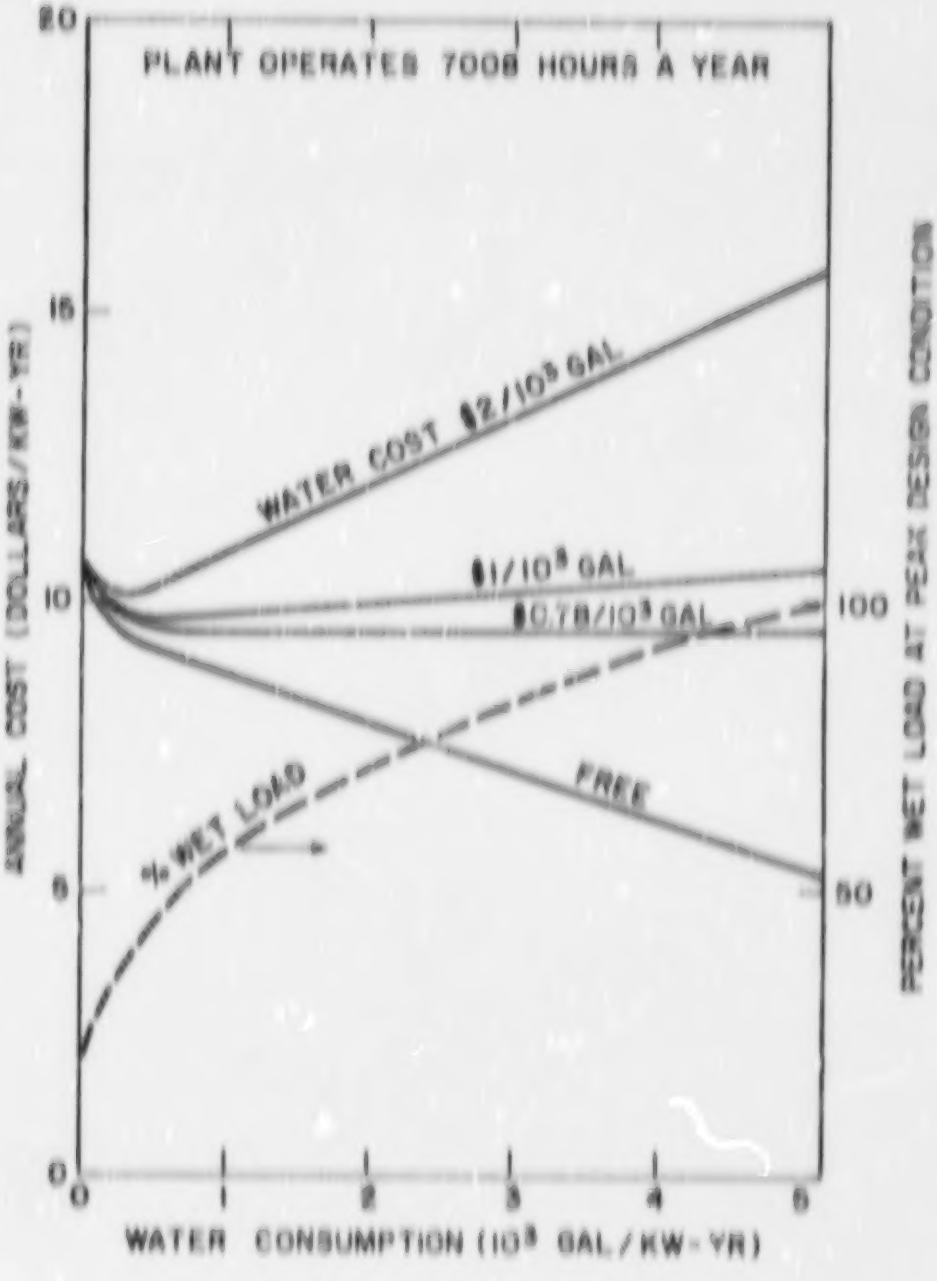


Figure 10-9. Annual cost of steam turbine condenser cooling at Farmington, New Mexico.

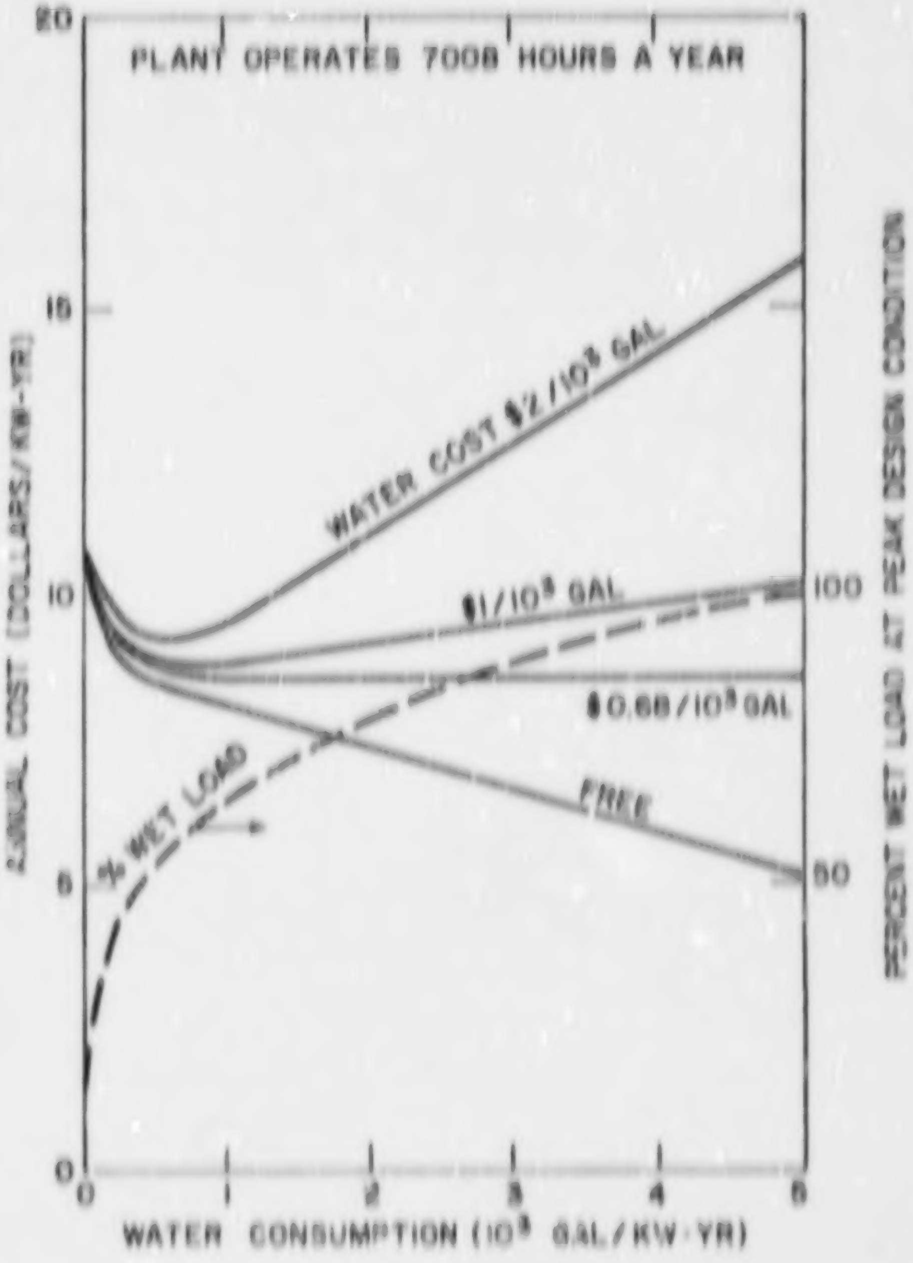


Figure 10-10. Annual cost of steam turbine condenser cooling at Beulah, North Dakota.

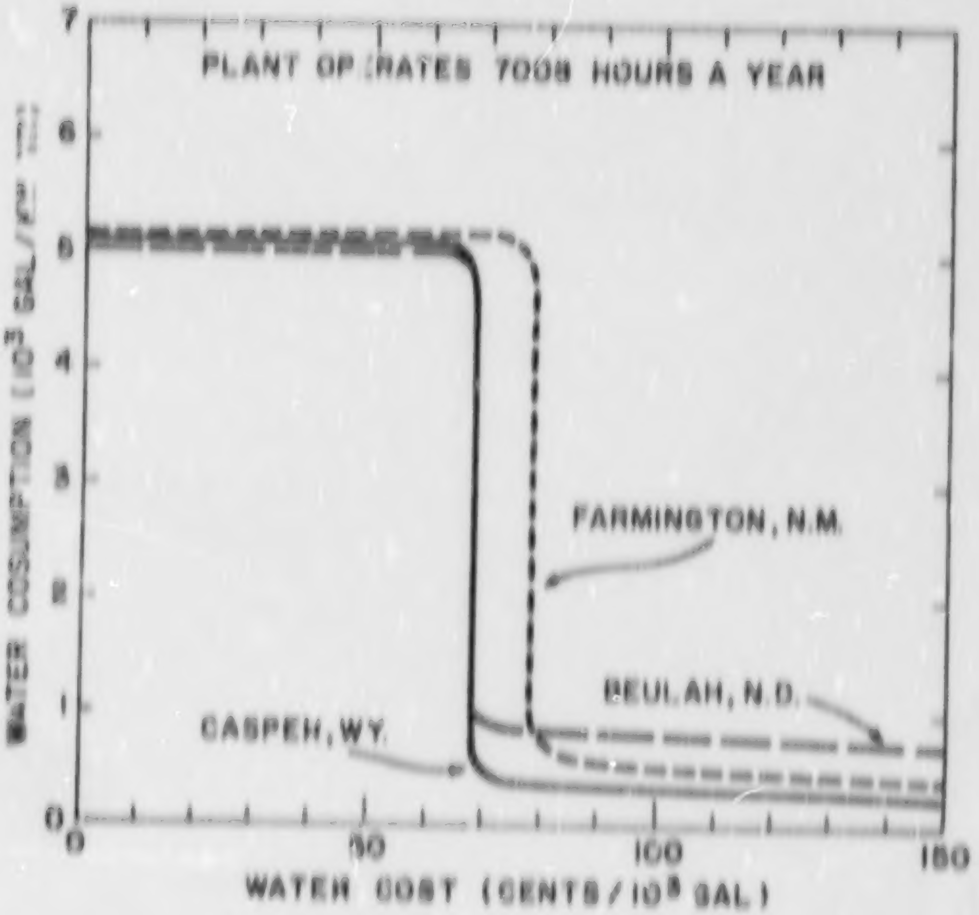
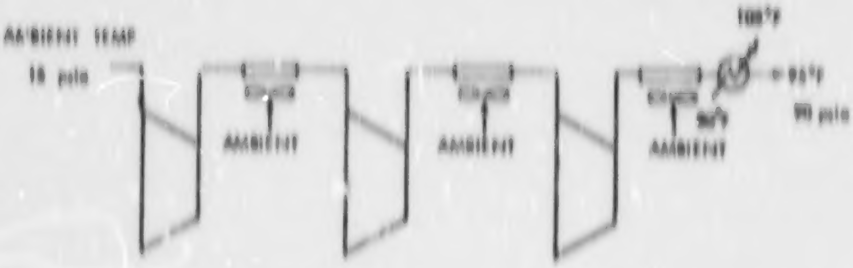
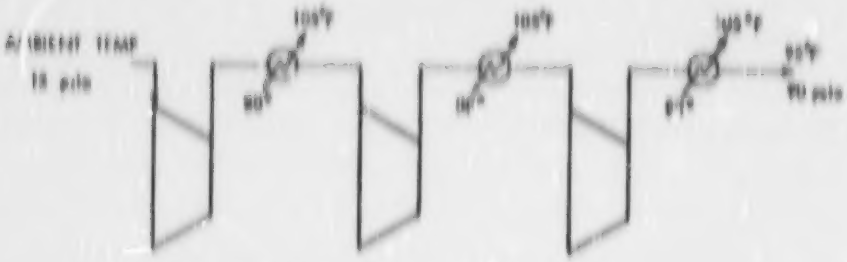


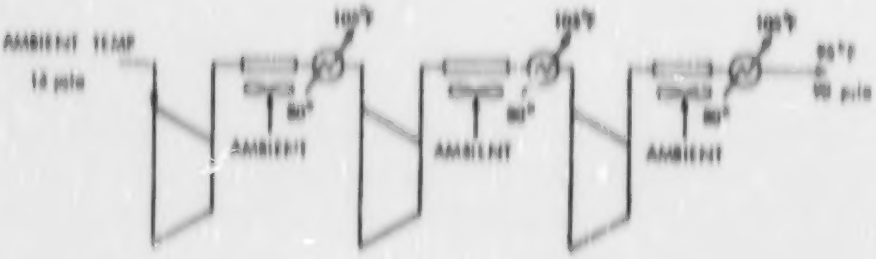
Figure 10-11. The effect of water cost on water consumed for cooling turbine condensers.


AMBIENT TEMP
15 psia
AMBIENT
AMBIENT
AMBIENT
100°F
95°F
90°F
90 psia

3 STAGE AIR COOLED AIR COMPRESSOR


AMBIENT TEMP
15 psia
100°F
80°
100°F
100°F
95°F
90 psia

3 STAGE WATER COOLED AIR COMPRESSOR


AMBIENT TEMP
14 psia
100°F
80°
AMBIENT
100°F
80°
AMBIENT
100°F
80°
AMBIENT
95°F
90 psia

3 STAGE AIR COOLED FOLLOWED BY WATER COOLED AIR COMPRESSOR

Figure 10-12. Compressor interstage cooling example.

air must be reduced to 95°F before being admitted to the separation plant. Table 10-9 gives the basis, the design conditions and the size of the resultant compressor at New Mexico and at Wyoming for the wet and dry cases. The capital cost of the installed compressors is $135/installed hp, plus $18/ft^2 installed dry heat transfer area, plus $5.1/ft^2 installed wet heat transfer area, plus $7/gpm circulated for the cooling tower.

In operation each stage of the compressor is assumed to be regulated at the design pressure ratio and thus to consume less than design energy when the temperature of gas entering the stage is below design temperature. For the climates of New Mexico and Wyoming, month-by-month calculations were made on the wet and on the dry systems to find the horsepower drawn by the compressor and the water evaporated in the cooling tower. The results are shown on Tables 10-10 and 10-11. The annual average compressor horsepower and the annual total water evaporation rate were found. The operating costs, also shown on Tables 10-10 and 10-11, were calculated as 18 percent of capital/yr for compressors, 17 percent of capital/yr for dry area, 20 percent of capital/yr for wet area and cooling tower (these percentages cover amortization and maintenance), and also 1.74¢/hp-hr ($2/10^6 Btu) for compressor drive steam and 1.49¢/hp-hr (2¢/kw-hr) for auxiliary energy to run the circulating water pumps and fans in dry coolers and cooling towers. It is clear that if the only choice were all wet or all dry, then wet cooling would be required at all sites. However, a combination of dry followed by wet cooling, as shown on Figure 10-12, is practical.

The wet/dry combination was also studied for the climate of New Mexico and Wyoming with the results shown on Tables 10-12 to 10-15 and Figures 10-13 and 10-14. When water costs $1.50 or more in New Mexico per thousand gallons evaporated, interstage cooling should be designed with dry cooling to 140°F followed by wet cooling to 95°F. The annual average water consumption will be 10.9 × 10^3 gallons compared to 116 × 10^3 gallons for all wet cooling. In Wyoming the change to wet/dry should be made when water costs about $1/thousand gallons evaporated. In fact, wet cooling has been used in New Mexico but combined dry/wet in Wyoming.

TABLE 10-9. BASIS AND DESIGN CONDITIONS FOR COMPRESSOR INTERSTAGE COOLING (ALL WET OR ALL DRY)

Basis: 2,000 lb/hr air compressed from 15 psia and ambient temperature to 90 psia and 95°F or less.

Design Conditions	New Mexico	Wyoming
Ambient temperature, °F	98	96
Entry to stages 2 & 3 when dry cooling, °F	140	140
Entry to stages 2 & 3 when wet cooling, °F	55	95
Design Compressor		
Dry cooling		
Total hp	82.3	82.2
Ft^2 dry area	136	131
Ft^2 wet area	28	28
Gal/min cooling water circulation	1.7	1.7
Wet cooling		
Total hp	78.1	78.0
Ft^2 wet area	206	206
Gal/min cooling water circulation	16.1	16.1

TABLE 13-11. SUMMARY OF COMPARISON ALL WET AND ALL DRY [illegible] COOLING RESULTS IN NEW MEXICO[a]

Month	Ambient Temp (F)	Cooling Tower Heat Removal Rate (Btu/lb water evaporated)	Compressor Operating Power (hp)		Evaporation Rate (10^3 gal/month)	
			Wet Cooling	Air Cooling	Wet Cooling	Air Cooling[a]
1	26	1,719	74.4	72.7	7.36	0
2	33	1,643	74.8	72.7	7.85	0
3	42	1,541	75.3	74.1	8.70	0
4	48	1,459	75.6	75.1	9.48	0
5	60	1,346	76.2	76.7	10.63	0.12
6	70	1,261	76.7	78.2	11.74	0.46
7	76	1,231	77.0	78.1	12.27	0.67
8	73	1,275	76.8	78.6	11.75	0.55
9	66	1,333	76.4	77.3	10.80	0.28
10	51	1,459	75.7	75.4	9.55	0
11	39	1,571	75.1	73.6	8.64	0
12	27	1,711	74.5	72.8	7.48	0
Annual average operating horsepower (hp):			75.7	73.4		
Annual total water evaporation rate (10^3 gal/yr):					116	2.08

Annual operating charges:

	Dollars/Year	
	Wet Cooling	Dry Cooling
Capital related costs	2,130.54	2,446.25
Compressor operating steam costs	10,538.51	10,484.16
Auxiliary energy costs	69.26	241.82
Total annual operating costs	12,738.77	13,170.23

For equal charges water cost $1.87/10^3$ gal.

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[a] Zero water evaporation means exit air temperature from the third air cooler is lower than 95°F so that the side water cooler is not operated.

TABLE 13-11. SUMMARY OF COMPARING ALL WET AND ALL DRY INTERSTAGE COOLING DESIGNS IN [illegible]

Month	Ambient Temp (F)	Cooling Tower Heat Removal Rate (Btu/lb water evaporated)	Compressor Operating Power (hp)		Evaporation Rate (10^3 gal/month)	
			Wet Cooling	Air Cooling	Wet Cooling	Air Cooling
1	24	1,659	74.35	71.56	7.37	0
2	26	1,651	74.46	71.85	7.46	0
3	33	1,643	74.75	72.74	7.86	0
4	41	1,561	75.22	74.07	8.67	0
5	54	1,451	75.88	76.22	9.80	0
6	65	1,340	76.44	77.65	10.87	0.36
7	71	1,289	76.75	78.53	11.53	0.55
8	70	1,295	76.69	78.38	11.47	0.51
9	59	1,371	76.13	76.76	10.46	0.25
10	47	1,501	75.52	74.96	9.20	0
11	33	1,643	74.87	72.74	7.86	0
12	30	1,647	74.75	72.44	7.78	0
Annual average operating horsepower (hp):			75.47	74.81		
Annual total water evaporation rate (10^3 gal/yr):					110.13	1.56

Annual operating charges:

	Dollars/year	
	Wet Cooling	Dry Cooling
Capital related costs	2,128.09	2,429.56
Compressor operating steam costs	10,505.02	10,413.21
Auxiliary energy costs	68.05	235.40
Total annual operating costs	12,701.13	13,078.17

For equal charges water costs $3.40/$10^3$ gal.

TABLE 10-12. DESIGN CONDITIONS FOR COMPRESSOR DRY-FOLLOWED-BY-WET INTERSTAGE COOLING IN NEW MEXICO

Basis: 2,000 lb/hr air compressed from 15 psia and ambient temperature to 90 psia and 95°F or less.

Design Conditions

Design temperature of air at exit of the dry cooler, °F:	140	160	180
Design ambient temperature, °F	98	98	98
Design entry to stages 2 and 3, °F	95	95	95
Design dry area, ft^2	115.5	76.1	48.7
Design wet area, ft^2	150.2	166.3	179.6
Design cooling water circulation, gpm	5.2	7.6	9.9
Design hp	78.1	78.1	78.1

TABLE 10-13. DESIGN CONDITIONS FOR COMPRESSOR DRY-FOLLOWED-BY-WET INTERSTAGE COOLING IN WYOMING

Basis: 2,000 lb/hr air compressed from 15 psia and ambient temperature to 90 psia and 95°F or less.

Design Conditions

Design temperature of air at exit of the dry cooler, °F:	140	160	180
Design ambient temperature, °F	96	96	96
Design entry to Stages 2 and 3, °F	95	95	95
Design dry area, ft^2	111.3	73.6	47.0
Design wet area, ft^2	150.2	166.3	179.6
Design cooling water circulation, gpm	5.2	7.6	9.9
Design hp	78.0	78.0	78.0

TABLE 10-14. SUMMARY OF COMPRESSOR DRY-FOLLOWED-BY-WET INTERSTAGE COOLING RESULTS IN NEW MEXICO

Basis: 2,000 lb/hr air compressed

At exit temperature of dry cooler (^{o}F):	140		160		180	
Month	Operating HP	Water Evap	Operating HP	Water Evap	Operating HP	Water Evap
1	72.4	0	73.9	1.1	74.7	2.6
2	73.4	0	74.5	1.4	75.4	3.0
3	74.8	0	75.5	1.9	75.2	3.8
4	75.9	0.4	76.2	2.3	75.5	4.3
5	76.4	1.2	76.1	3.3	76.1	5.3
6	76.6	2.2	76.6	4.2	76.6	6.2
7	76.9	2.7	76.9	4.7	76.9	6.7
8	76.7	2.4	76.7	4.3	76.8	6.3
9	76.8	1.5	76.3	3.6	76.3	5.5
10	76.1	0.5	75.7	2.5	75.6	4.4
11	74.4	0	75.1	1.7	75.1	3.5
12	72.5	0	74.0	1.1	74.8	2.7
Annual avg operating horsepower (hp):	75.3		75.6		75.7	
Annual total water evaporation rate (10^3 gal/yr):		10.9		32.1		54.3
Annual operating charges ($/yr):						
Capital related costs		2,411.44		2,310.59		2,243.55
Compressor operating steam costs		10,475.45		10,525.49		10,544.10
Auxiliary energy cost		5.96		18.56		32.01
Total annual operating cost		12,892.75		12,854.63		12,819.66

TABLE 10-15. SUMMARY OF COMPRESSOR DRY-FOLLOWED-BY-WET INTERSTAGE COOLING RESULTS IN WYOMING

Air exit temperature of dry cooler (°F):	140		160		180	
Month	Operating HP	Water Evap	Operating HP	Water Evap	Operating HP	Water Evap
1	72.3	0	73.7	1.1	74.6	2.7
2	72.6	0	73.9	1.2	74.8	2.8
3	73.5	0	74.5	1.4	75.4	3.1
4	74.8	0	75.5	1.9	75.1	3.8
5	76.0	1.0	75.8	2.9	75.8	4.8
6	76.4	1.8	76.3	3.8	76.3	5.7
7	76.7	2.4	76.6	4.3	76.7	6.2
8	76.6	2.3	76.6	4.2	76.6	6.2
9	76.4	1.3	76.0	3.3	76.0	5.2
10	75.7	0.4	76.1	2.2	75.4	4.0
11	73.5	0	74.5	1.5	75.4	3.1
12	73.2	0	74.3	1.4	75.2	3.0
Annual avg operating horsepower (hp):	74.8		75.3		75.6	
Annual total water evaporation rate (10^3 gal/yr):		9.2		29.3		50.6
Annual operating charges ($/yr):						
Capital related costs		2,396.43		2,300.56		2,235.93
Compressor operating steam costs		10,431.61		10,485.81		10,526.62
Auxiliary energy cost		5.12		17.53		30.85
Total annual operating cost		12,815.16		12,803.89		12,793.39

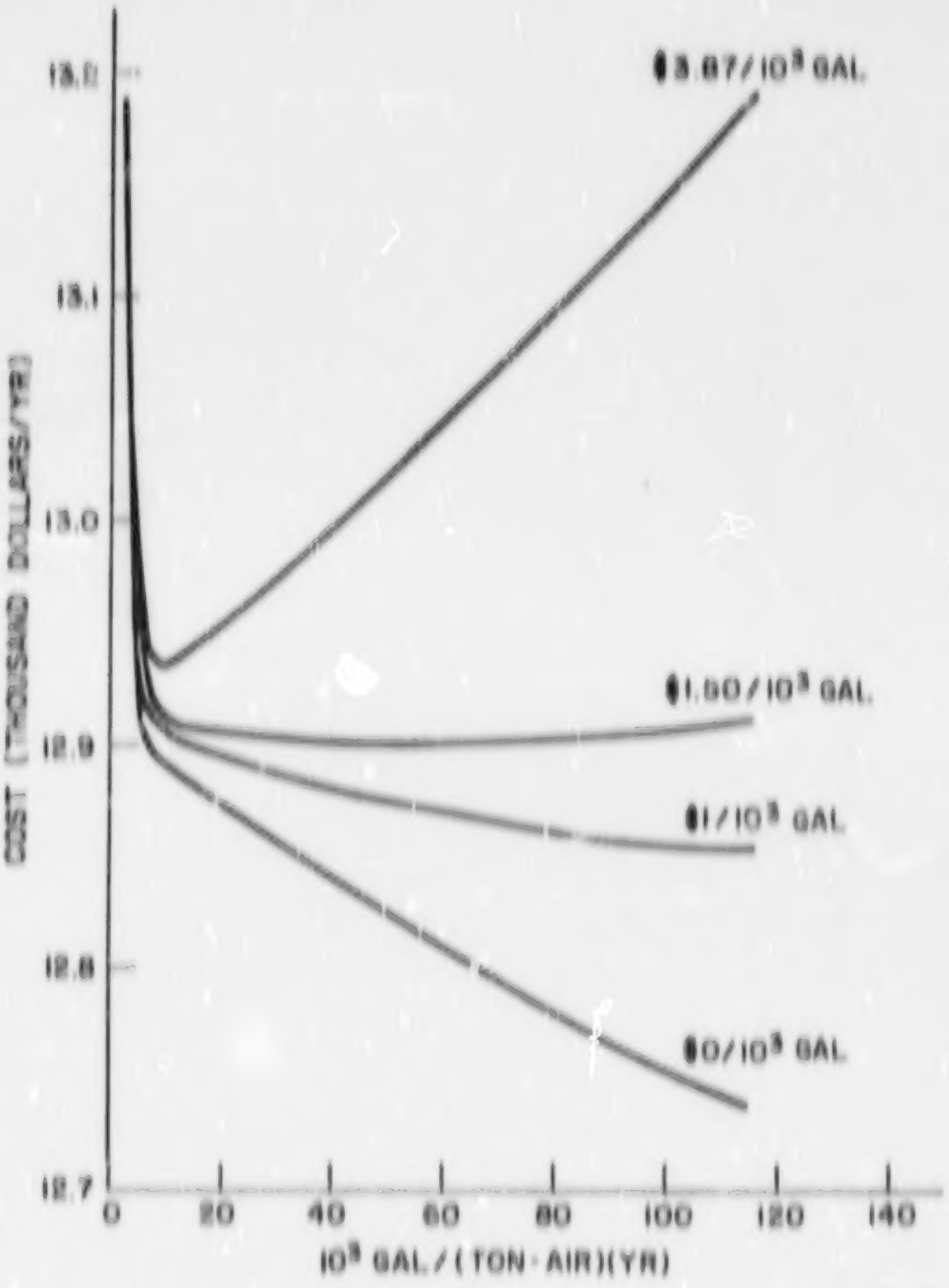

Figure 10-11. Operating cost of air compressor interstage cooling in New Mexico (2000 lb/hr air).

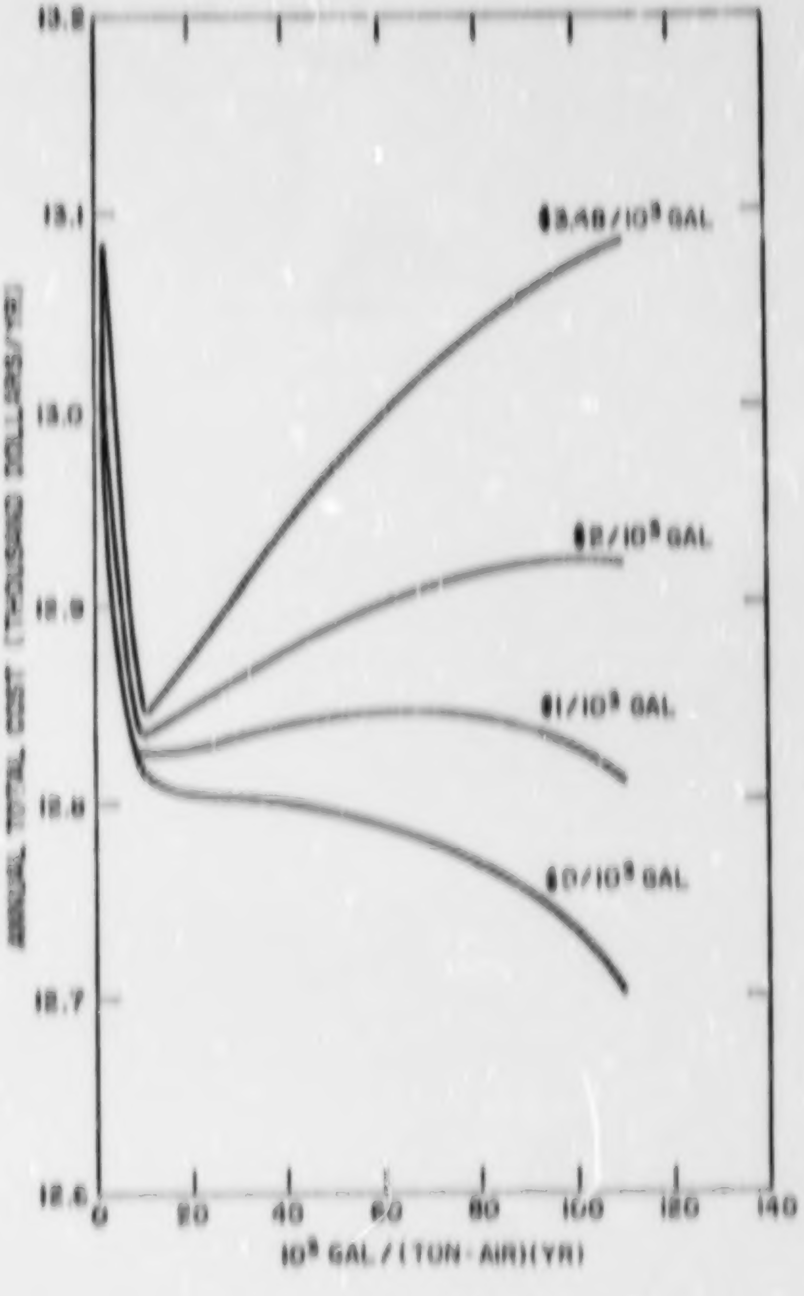

Figure 10-14. Operating cost of air compressor interstage cooling in Wyoming (2000 lb/hr air).

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SECTION 11

WATER FOR MINE COMPLEX AND OTHER OFF-SITE USES

11.1 INTRODUCTION AND SUMMARY OF RESULTS

In this section is presented the general methodology for calculating the amount of water consumed in the mining of coal and in any subsequent land reclamation required. The water quantities for this category of usage generally will not be too strongly affected by the choice of conversion process, except as it determines the actual quantity of material to be mined. However, the mine location and whether the mining is surface or underground will be strong determinants of the quantity of water consumed. At all the sites studied, surface mining is used.

The categories of water use are shown on Tables 11-1 to 11-3 with the estimates made in the following paragraphs.

11.2 ROAD, MINE AND EMBANKMENT DUST CONTROL

Fugitive dust generated on haul roads and unpaved areas in the neighborhood of the mine such as the mine benches and overburden placement areas must be controlled. The length of unpaved haul roads and mine bench areas depends on the mine productivity, as measured by the amount of coal recoverable per unit area of stripped land. In the present study the following mine yields are used:

Location	10^3 lb/acres
Beulah, North Dakota[3]	50,000
Gillette, Wyoming[1,2]	180,000
Navajo, New Mexico[4]	74,000

TABLE 11-1. CALCULATION OF WATER FOR MINE COMPLEX IN WYOMING

Units: 10^3 lb/hr

	Hygas	Synthane	SRC	Power
Coal mined	1,527	1,918	1,916	1,570
Water for road & mine dust control	13	16	16	13
Water for handling & dust control	31	38	39	31
Sanitary & potable water	1.7	1.7	1.7	1.7
Service & fire water	2.6	2.6	2.6	2.6
Sewage returned[a]	303	303	303	303
Revegetation	0	0	0	0

[a] Includes sewage from satellite town.

TABLE 11-2. CALCULATION OF WATER FOR MINE COMPLEX IN NORTH DAKOTA

Units: 10^3 lb/hr

	Hygas	SRC	Power
Coal mined	2,108	2,380	1,990
Water for road & mine dust control	52	59	49
Water for handling & dust control	42	47	40
Sanitary & potable water	2.0	2.0	2.0
Service & fire water	3.0	3.0	3.0
Sewage returned	1.5	1.5	1.5
Revegetation	0	0	0

TABLE 11-3. CALCULATION OF WATER FOR MINE COMPLEX IN NEW MEXICO

Units: 10^3 lb/hr

	Hygas	SRC	Power
Coal mined	1,505	1,853	1,470
Water for road and mine dust control	34	44	33
Water for handling and dust control	30	39	29
Sanitary and potable water	2.6	7.6	2.6
Service and fire water	3.9	3.9	3.9
Sewage returned	1.8	1.8	1.8
Revegetation	46	60	45

In the assumed mine model the mining of 100 acres per year would require 2 miles of 45 ft wide unpaved haul roads to serve as spurs to conveyor belts that would feed the coal to the plant. Such a belt line operation is described in Reference 1. The bench area acreage that would have to be wet down is approximately equal to four times the daily acreage that is mined. The sum of the two unpaved areas determines the area where dust control must be practiced. This area is 5,320 ft^2/(acre mined/yr).

The simplest means of holding down fugutive dust is to wet down the mine area and haul roads. It is assumed that the roads and mine area can be kept in a wetted condition through an annual deposition of water equal to the net annual evaporation rate. Any rainfall is taken to be an additional safety factor. The annual pond evaporation rates for the areas examined are:

Location	Inches/year
Beulah, North Dakota	45
Gillette, Wyoming	54
Navajo, New Mexico	61

The lay-down rate can be calculated from the relation,

lay-down rate = disturbed area × evaporation rate

That is, for 10^3 lb coal mined,

$$\begin{aligned}\text{lay-down rate, lb} &= (10^3 \text{ lb coal}) \times (\text{acres mined}/10^3 \text{ lb coal}) \\ &\times (5230 \text{ ft}^2 \text{ wetted}/(\text{acre mined/yr})) \times (1 \text{ ft}/12 \text{ inches}) \\ &\times (\text{wetting rate, inches/yr}) \times (62.4 \text{ lb water/ft}^3)\end{aligned}$$

This equation gives

Location	Water for road, mine and embankment dust control (lb water/10^3 lb coal)
Beulah, North Dakota	24.5
Gillette, Wyoming	8.2
Navajo, New Mexico	22.4

For most of the processes the coal mining rate is equal to the coal utilization rate as given in the various process description sections. However, because the Lurgi gasifiers cannot accept fines, the coal mining rate for the power plants is equal to 1.2 times the utilization rate. The fines are assumed to be sold.

11.3 HANDLING AND CRUSHING DUST CONTROL

The water needs associated with the preparation of the coal are a part of the estimate of the water requirements for a mining operation integrated with a synthetic fuel plant. In all coal preparation plants dust is generated in the stages of loading and unloading, breaking, conveying, crushing, general screening and storage. The water required to hold down this dust will be considered here.

The ways of preventing dust from becoming airborne are through the application of water sprays or of nontoxic chemicals and the use of dry or wet dust collectors with partial or total enclosure. It is assumed that the principal dust generating sources will be enclosed and that where feasible, air will be circulated and dry bag dust collection employed. Whenever coal pulverization is necessary this will be done under conditions of total enclosure with no fugitive dust or hold-down water requirements. In inactive storage the use of water for holding down dust can be minimized by the use of nontoxic chemicals.

Despite the design precautions indicated, in large-scale plants with many transfer points, transfer belts, surge bins, storage silos and active storage sites it is necessary to employ water sprays to wet down the coal. This is also generally necessary with breaking and primary crushing operations. An examination of the Wesco Lurgi plant design[4] and the TOSCO oil shale plant design[5] indicates that a consumptive use of 1 lb of water for every 50 lbs of coal handled and crushed is a reasonably conservative estimate.

11.4 SANITARY AND POTABLE WATER

A number of water requirements in the mine are a direct function of the number of people employed in the mine. One such obvious requirement is water for sanitary needs and potable usage. Of course the number of personnel is related to the tonnage mined, but the number will also depend on the mine type and location.

In fact, the quantity of coal used for each plant is sufficiently similar, and the water requirements dependent on people are sufficiently small that the requirements may be taken to be independent of the process.

Location	Mine Personnel (any plant)
North Dakota	270
Wyoming	230
New Mexico	300

The water used per man-shift and the fraction of that water which is not recovered as sewage is dependent to some extent on the climate, and we have used

Location	Sanitary and potable water used (gallons/man-shift)	Consumed (% of used)
Wyoming, North Dakota	30	25
New Mexico	35	30

The average hourly water rates have been calculated from the following formula and entered onto Tables 11-1 to 11-3

$$\text{Water used, lb/hr} = (\text{number of men}) \times (\text{gallons/man-shift}) \times (5\ \text{shifts/week}) \times (1\ \text{week}/168\ \text{hrs}) \times (8.33\ \text{lb/gallon})$$

11.5 SERVICE AND FIRE WATER

The service water usage in the mine such as for equipment washing, maintenance, pump seals, etc., along with the fire water usage through evaporation loss, is a difficult quantity to estimate. However, an analysis of a number of mine designs indicates that this usage is essentially nonrecoverable and can be related to the usage of sanitary and potable water.

The estimated ratio for service to sanitary usage for a proposed 10×10^6 ton/yr surface mine near Gillette is about 1.6.[6] This same figure for the proposed Kaiparowits undergound mine[7] is about 1.3, based on estimated sanitary water usage. The two values are sufficiently close that the average service water usage for the mine is 1.5 times the sanitary water usage. Moreover, all of the water is taken to be consumed since recovery in the mine work areas would prove quite difficult.

11.6 REVEGETATION

As part of any reclamation of mined land in arid and semi-arid regions, there exists a potential requirement for supplemental irrigation water associated with the establishment of soil stabilizing plant cover on mine spoils.

It is concluded that coal mined areas with greater than 10 inches of mean annual precipitation can be reclaimed without supplemental irrigation.[8] Where there is less than 10 inches of annual rainfall, partially reshaped coal mine spoils can be successfully revegetated with supplemental irrigation of about 10 inches during the first growing season, with no further requirement during subsequent growing seasons.[9] Only at the Navajo, New Mexico site is irrigation for revegetation required. The water requirement can be calculated from the following formula:

$$\begin{aligned}\text{revegetation water, lb/hr} = {} & (\text{lb coal/hr}) \times (\text{acres mined}/74 \times 10^6\ \text{lb coal}) \\ & \times (10\ \text{inches water}) \times (43{,}560\ \text{ft}^2/\text{acre}) \\ & \times (1\ \text{ft}/12\ \text{inches}) \times (62.4\ \text{lb/ft}^3)\end{aligned}$$

Revegetation water in New Mexico =

$$30.6\ \text{lb water}/10^3\ \text{lb coal}$$

11.7 SATELLITE TOWN

At the Wyoming site (for an exemplary study) the process plants take in the sewage water from a satellite town. The total employment in mine and plant is about 1,000 people (see also Section 12) and the town will have a population of about 7,000 people. According to Reference 10 the average daily per capita water requirement in Wyoming is 175 gallons, of which 50 gallons are consumed and 125 gallons are recovered as sewage. About 0.87×10^6 gallons sewage/day is treated for plant intake water.

REFERENCES SECTION 11

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SECTION 12

ADDITIONAL ON-SITE WATER STREAMS

12.1 INTRODUCTION AND SUMMARY OF RESULTS

In this section is presented the method of calculating the remaining plant water streams not discussed elsewhere. The results are presented on Tables 12-1 to 12-3.

12.2 EVAPORATION

For the particular source waters chosen for this study a settling basin, which is subject to evaporative losses, is not required. However, all plants require a reservoir from which evaporation will occur. Net evaporation rates (pond evaporation minus precipitation) are

	Net evaporation (in/yr)	
	No control	With control
North Dakota	30	23
Wyoming	40	30
New Mexico	53	40

The net evaporation rate with control assumes some form of evaporation control such as the application of monomolecular films to the water surface. This control may also be a natural one resulting from the presence of impurities in the local waters. Experience indicates that a reasonable maximum value to take for the effective reduction in the evaporation minus precipitation rate is 25 percent.[1]

TABLE 12-1. CALCULATION OF ADDITIONAL WATER IN WYOMING

	Hygas	Synthane	SRC	Power
Reservoir volume, 10^6 gallons	36.5	36.5	36.5	50.
Total bottom ash 10^3 lb/hr	102	27	114	74
10^9 Btu/hr	0.053	0.02	0.07	0.06
fly ash 10^3 lb/hr	10	109	0	0
	Water Requirements 10^3 lb/hr			
Reservoir Evaporation	2.9	2.9	2.9	4.0
Water for ash disposal	86	55	104	82
Water for in-plant dust contol	15	19	10	13
Service and fire water	9.6	9.6	9.6	9.6
Sanitary and potable water	4.8	4.4	4.8	4.8
Sewage returend	9.8	9.8	9.8	9.8

TABLE 12-2. CALCULATION OF ADDITIONAL WATER IN NORTH DAKOTA

		Hygas	SRC	Power
Reservoir volume	10^6 gallons	45	20	50
Total bottom ash	10^3 lb/hr	116	130	86
	10^9 Btu/hr	0.06	0.07	0.08
Fly ash	10^3 lb/hr	15	0	0
		Water requirements 10^3 lb/hr		
Reservoir evaporation		3.6	2.1	4.0
Water for ash disposal		98	107	119
Water for in-plant dust control		21	23	17
Service and fire water		9.6	9.6	9.6
Sanitary and potable water		4.8	4.8	4.8
Sewage returned		9.8	9.8	9.8

TABLE 12-3. CALCULATION OF ADDITIONAL WATER IN NEW MEXICO

		Hygas	SRC	Power
Reservoir volume, 10^6 gallons		45	20	60
Total bottom ash	10^3 lb/hr	226	265	165
	10^9 Btu/hr	0.125	0.13	0.16
fly ash	10^3 lb/hr	22	0	0
		Water requirements 10^3 lb/hr		
Reservoir evaporation		4.8	2.1	6.1
Water for ash disposal		198	229	190
Water for in-plant dust control		15	20	12
Service and fire water		11.2	11.2	11.2
Sanitary and potable water		5.6	5.6	5.6
Sewage returned		11.2	11.2	11.2

At North Dakota and New Mexico the reservoir will hold the amount shown on Tables 12-2 and 12-3, which is about one week's supply. At Wyoming, where water is particularly scarce, the reservoir for the fuel plants will hold six weeks' supply of treated sewage from the satellite town, that is, 36.5×10^6 gallons. For the power plant a large reservoir is used. Evaporation control will be practiced at Wyoming and New Mexico, where it is particularly important, and will be assumed not to be practiced in North Dakota. The reservoirs are assumed to be 30 feet deep, and the evaporation rates have been calculated from the following formula and entered onto Tables 12-1 and 12-3.

$$\begin{aligned}\text{Reservoir evaporation, lb/hr} = {} & \text{(reservoir capacity, gal)} \\ & \times \text{(8.33 lb/gal)} \times \text{(1/30 ft depth)} \\ & \times \text{(net evaporation, in/yr)} \\ & \times \text{(1 ft/12 in)} \times \text{(1 yr/8760 hrs)}\end{aligned}$$

$$\begin{aligned}\text{Reservoir evaporation, lb/hr} = {} & 2.64 \times 10^{-6}\ \text{(reservoir capacity, gal)} \\ & \times \text{(net evaporation, in/yr)}\end{aligned}$$

12.3 ASH DISPOSAL

The ash which enters the plants with the coal leaves in two forms called bottom ash and fly ash or top ash. In the power plants all the ash leaves as bottom ash from the Lurgi gasifiers. In the SRC plants all the ash is assumed to be bottom ash from the Koppers-Totzek gasifiers (in this case some of the ash is recovered from the gas but is treated as bottom ash). In the Synthane plant all the ash remains in the char fed to a boiler. In this boiler, which is assumed to be similar to a pulverized coal fired dry-ash furnace, 20 percent of the ash leaves as bottom ash and 80 percent leaves as fly ash.[2] In the Hygas plants most of the ash leaves the bottom of the gasifier. However, these plants also have coal fired furnaces in which 20 percent of the ash leaves as bottom ash and 80 percent as fly ash.

Water is used in bottom ash disposal to quench the ash and leave it wet to avoid dusting in transportation to the disposal site. In each detailed process description is given the enthalpy of bottom ash leaving the plant. (For the Hygas plant gasifier ash residues sensible heats were obtained by subtracting the higher heating value from the heating values tabulated.) This enthalpy is measured above 77°F and it is only necessary to quench the ash to about 200°F. Nevertheless, the quench water requirement has been conservatively estimated using the stated enthalpies of bottom ash and taking 1000 Btu/lb water evaporated in quenching. It is also assumed that 0.3 lb water remains in each pound of bottom ash to prevent dusting, so the wet ash leaves as 23 wt percent moisture.

Fly ash is assumed to be recovered from flue gases using dry electrostatic precipitators ahead of the flue gas desulfurization scrub. The removal process is dry, but when the ash is withdrawn from storage hoppers or silos, water is sprayed into the screw conveyers to prevent dusting. The water spray rate is 0.25 lb/lb dry ash so the wet fly ash leaves as 20 wt percent moisture.

12.4 IN-PLANT DUST CONTROL

Within the boundaries of any of the plants considered in the present study, water will be needed for dust control at a certain number of points. These points are similar to those described for the mines, namely, transfer areas, active storage, surge bins, etc.

Somewhat less water would be required in the plants than in the mines, since many of the operations tend to be enclosed. On this basis a good assumption is a consumptive use of one half that applicable to the mine areas, specifically 1 lb of water for every 100 lbs of coal handled and transferred. This is a little less water than that deduced from the data of Reference 3.

12.5 SANITARY, SERVICE AND FIRE WATER

These requirements are calculated as for the mine complex described in Section 11. The plants each employ about 650 people (References 3 to 7). Service and fire water is assumed here to be two times the sanitary and potable water for plants, of which 85 percent of the water is assumed to be returned as sewage.

REFERENCES SECTION 12

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SECTION 13

SITE STUDIES - 1: WATER CONSUMPTION

For convenience in designing water treatment plants, all the water quantity figures have been assembled on Tables 13-1 to 13-10. Except for cooling water the quantities have been copied directly from Sections 5 to 9, 11 and 12. Cooling water is discussed below.

The steam turbine condensers for electric power generation will be wet cooled in North Dakota and New Mexico and wet/dry in Wyoming. The wet cooling loads can be found on Table 9-3 as the sum of the "process streams cooled by water" and the "steam turbine condenser." The cooling rates on the tower are those shown on Table 9-11 and in Section 9.6.

In North Dakota, for Hygas and SRC, the water is assumed to be cheap and available. The wet cooling load is taken from the tables of ultimate disposition of waste heat and is the sum of the "wet cooling of plant process streams," "total steam turbine condensers," "total compressor interstage cooling," plus 10 percent of the "acid gas removal regenerator condenser" load (as explained in Section 10.5). The cooling rate is taken from Table 10-2.

In New Mexico, for exemplary purposes the water is taken to be available but salty. Furthermore, because of the salt, it is assumed cooling tower blowdown cannot be admixed with ash for disposal but must be separately concentrated and disposed of in a segregated, lined evaporation pond. This pushes the cost of cooling water to well over 78¢/thousand gallons evaporated. Therefore, from Section 10, the steam turbine condensers will be designed to be about 45 percent wet and 55 percent dry at the summer design condition. The annual average water consumption is 10 percent of the all wet case.

In Wyoming water has been assumed to be very expensive if more than the quantity of municipal sewage is used. All the tables for Wyoming show this municipal sewage under the heading "sewage return." Maximum water conservation will be practiced. The annual average water consumption for turbine condensers will be 10 percent of the all wet case. The annual average water consumption for interstage cooling on gas compressors will also be 10 percent of the all wet case. For the Synthane plant the acid gas removal is a Benfield type and only dry condensing is used.

To record the net water used a formal loss has been taken of 7 percent of those streams requiring ammonia separation and 1 percent of those streams requiring biotreatment. A formal loss has been taken of 5 percent of the water entering boiler feed water treatment in North Dakota and Wyoming, and 10 percent loss in New Mexico where the water is brackish. Clean condensate and other waters requiring flashing are assumed to have a 1 percent loss. These are formal and approximate loss figures, and small differences will occur from plant to plant. The effect of these losses on water consumption is less than 5 percent.

Net water consumption is shown on Figure 8-1. Much of the most important variation is in cooling water. This requirement is higher in the power plants than in the fuel plants simply because the power plants are less efficient. In the power plants the load on wet cooling was reduced in Wyoming over North Dakota and New Mexico because of the great expense of water, and the result on total water consumption is to reduce it to about one half. In the fuel plants the load on wet cooling was successively reduced from North Dakota to New Mexico to Wyoming resulting in large changes in total water consumption.

For the fuel plants the process water consumption depends on the process, because all take in dried coal. All the SRC plants are net producers of process water: the product fuel contains no more hydrogen than the coal. The gas plants all consume water in the process as a source of hydrogen. The Synthane process uses less water than the Hygas because all the coal entering the plant passes through the gasifier and contributes its hydrogen. On the other hand, flue gas desulfurization water, assumed to be required only in the gas plants, is higher in Synthane than in Hygas because bone dry char is burnt to raise steam. Much of the water consumed in wet flue gas desulfurization is vaporized to saturate the flue gas.

The power plants use Lurgi technology and take in wet coal. The process water consumption is a reflection of the moisture content of the coal. Where the coal is wet, as at North Dakota, consumption is low; where the coal is dry, as at New Mexico, consumption is higher.

The water consumed for dust control and ash disposal is mostly a fraction of the ash content of the coal and is highest in New Mexico for all plants.

TABLE 11-1. APPROXIMATE WATER REQUIREMENTS

Plant Electric Site North Dakota

Plant Size 10^6 kilowatts

(Note that all water rates are for on-stream times. In calculating annual average multiply by stream factor.)

	10^3 lb/hr	10^6 gal/day
PROCESS		
Boiler feed water into process	943	2.72
Foul water out of process	986	2.84
COOLING		
Water evaporated for cooling	2470	7.12
FLUE GAS DESULFURIZATION	0	
MINE AND OFF-SITE		
Road, mine and embankment dust control	49	0.14
Handling and crushing dust control	40	0.12
Sanitary and potable water	2	0.01
Service and fire water	3	0.01
Sewage returned	1.5	0.00
Revegetation	0	0
ADDITIONAL ON-SITE STREAMS		
Reservoir evaporation	4.0	0.01
Ash disposal	119	0.34
Dust control	20	0.06
Sanitary and potable water	4.8	0.01
Service and fire water	9.6	0.03
Sewage returned	9.8	0.03
NET WATER USED		
(See Text)	2840	8.2

TABLE 13-2. APPROXIMATE WATER REQUIREMENTS

Plant Hygas-SNG Site North Dakota

Plant Size 230×10^6 scf/day ; 10.09×10^9 Btu/hr

(Note that all water rates are for on-stream times. In calculating annual average multiply by stream factor.)

	10^3 lb/hr	10^6 gal/day	gal/10^6 Btu product
PROCESS			
Boiler feed water into process	1,015	2.92	12.06
Foul water out of process	294	0.85	3.50
Clean water out of process	201	0.58	2.39
COOLING			
Water evaporated for cooling	790	2.27	9.40
FLUE GAS DESULFURIZATION	68	0.20	0.81
MINE AND OFF-SITE			
Road, mine and embankment dust control	52	0.15	0.62
Handling and crushing dust control	42	0.12	0.50
Sanitary and potable water	2.0	0.01	0.02
Service and fire water	3.0	0.01	0.04
Sewage returned	1.5	0.00	0.02
Revegetation	0	0	0
ADDITIONAL ON-SITE STREAMS			
Reservoir evaporation	3.6	0.01	0.04
Ash disposal	98	0.28	1.17
Dust control	21	0.06	0.25
Sanitary and potable water	4.8	0.01	0.06
Service and fire water	9.6	0.03	0.11
Sewage returned	9.8	0.03	0.12
NET WATER USED			
(See Text)	1680	4.8	20.0

TABLE 11-3. APPROXIMATE WATER REQUIREMENTS

Plant Solvent Refined Coal Site North Dakota

Plant Size 10,000 tons/day ; 11.34 x 10^9 Btu/hr

(Note that all water rates are for on-stream times. In calculating annual average multiply by stream factor.)

	10^3 lb/hr	10^6 gal/day	gal/10^6 Btu product
PROCESS			
Boiler feed water into process	944	2.72	8.49
Foul water out of process (1)	323	0.93	2.91
Water from gas purification	323	0.93	2.91
Water from gasification train	177	0.51	1.59
Clean water out of process	177	0.51	1.59
COOLING			
Water evaporated for cooling	880	2.54	7.91
FLUE GAS DESULFURIZATION	0		
MINE AND OFF-SITE			
Road, mine and embankment dust control	59	0.17	0.53
Handling and crushing dust control	47	0.14	0.42
Sanitary and potable water	2.6	0.01	0.02
Service and fire water	3.9	0.01	0.04
Sewage returned	1.8	0.01	1.62
Revegetation	0	0	0
ADDITIONAL ON-SITE STREAMS			
Reservoir evaporation	2.1	0.01	0.02
Ash disposal	107	0.31	0.96
Dust control	24	0.07	0.22
Sanitary and potable water	4.8	0.01	0.04
Service and fire water	9.6	0.03	0.09
Sewage returned	9.8	0.03	0.09
NET WATER USED			
(See Text)	1150	3.3	10.4

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(1) Section 7.4, not Table 7-1.

TABLE 13-4. APPROXIMATE WATER REQUIREMENTS

Plant Electric Site New Mexico

Plant Size 10^6 kilowatts ;

(Note that all water rates are for on-stream times. In calculating annual average multiply by stream factor.)

	10^3 lb/hr	10^6 gal/day
PROCESS		
Boiler feed water into process	970	2.79
Foul water out of process	625	1.80
COOLING		
Water evaporated for cooling	2476	7.13
FLUE GAS DESULFURIZATION	0	
MINE AND OFF-SITE		
Road, mine and embankment dust control	33	0.10
Handling and crushing dust control	29	0.08
Sanitary and potable water	2.6	0.01
Service and fire water	3.9	0.01
Sewage returned	1.8	0.01
Revegetation	45	0.13
ADDITIONAL ON-SITE STREAMS		
Reservoir evaporation	6.3	0.02
Ash disposal	190	0.48
Dust control	15	0.04
Sanitary and potable water	5.6	0.02
Service and fire water	11.2	0.03
Sewage returned	11.2	0.03
NET WATER USED		
(See Text)	1400	10.2

TABLE 13-5. APPROXIMATE WATER REQUIREMENTS

Plant Hygas-SNG site New Mexico

Plant Size 250 x 10^6 scf/day ; 10.09 x 10^9 Btu/hr

(Note that all water rates are for on-stream times. In calculating annual average multiply by stream factor.)

	10^3 lb/hr	10^6 gal/day	gal/10^6 Btu product
PROCESS			
Boiler feed water into process	1,015	2.92	12.08
Foul water out of process	294	0.85	3.50
Clean water out of process	201	0.58	2.39
COOLING			
Water evaporated for cooling	389	1.12	4.63
FLUE GAS DESULFURIZATION	108	0.31	1.28
MINE AND OFF-SITE			
Road, mine and embankment dust control	34	0.10	0.40
Handling and crushing dust control	30	0.09	0.36
Sanitary and potable water	2.6	0.01	0.03
Service and fire water	3.9	0.01	0.05
Sewage returned	1.8	0.01	0.02
Revegetation	46	0.13	0.55
ADDITIONAL ON-SITE STREAMS			
Reservoir evaporation	4.8	0.01	0.06
Ash disposal	198	0.57	2.36
Dust control	15	0.04	0.18
Sanitary and potable water	5.6	0.02	0.07
Service and fire water	11.2	0.03	0.13
Sewage returned	11.2	0.03	0.13
NET WATER USED			
(See Text)	1491	4.3	17.8

TABLE 11-6. APPROXIMATE WATER REQUIREMENTS

Plant Solvent Refined Coal Site New Mexico

Plant Size 10,000 tons/day ; 13.34×10^9 Btu/hr

(Note that all water rates are for on-stream times. In calculating annual average multiply by stream factor.)

	10^3 lb/hr	10^6 gal/day	gal/10^6 Btu product
PROCESS			
Boiler feed water into process	639	1.84	5.75
Foul water out of process (1)	215	0.62	1.94
Water from gas purification	250	0.72	2.25
Water from gasification train	160	0.46	1.44
Clean water out of process	49	0.14	0.44
COOLING			
Water evaporated for cooling	297	0.86	2.67
FLUE GAS DESULFURIZATION	0		
MINE AND OFF-SITE			
Road, mine and embankment dust control	44	0.13	0.40
Handling and crushing dust control	39	0.11	0.35
Sanitary and potable water	2.6	0.01	0.02
Service and fire water	3.9	0.01	0.04
Sewage returnud	1.8	0.01	0.02
Revegetation	60	0.17	0.54
ADDITIONAL ON-SITE STREAMS			
Reservoir evaporation	2.1	0.01	0.02
Ash disposal	165	0.48	1.48
Dust control	12	0.03	0.11
Sanitary and potable water	5.6	0.02	0.05
Service and fire water	11.2	0.03	0.10
Sewage returned	11.2	0.03	0.10
NET WATER USED			
(See Text)	665	1.9	6.0

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(1) Section 7.4, not Table 7-1

TABLE 11-7. APPROXIMATE WATER REQUIREMENTS

Plant Electric Site Wyoming

Plant Size 10^6 kilowatts

(Note that all water rates are for on-stream times. In calculating annual average multiply by stream factor.)

	10^3 lb/hr	10^6 gal/day
PROCESS		
Boiler feed water into process	957	2.76
Foul water out of process	720	2.07
COOLING		
Water evaporated for cooling	989	2.85
FLUE GAS DESULFURIZATION	0	
MINE AND OFF-SITE		
Road, mine and embankment dust control	13	0.04
Handling and crushing dust control	31	0.09
Sanitary and potable water	1.7	0.00
Service and fire water	2.6	0.01
Sewage returned*	303	0.88
Revegetation	0	0
ADDITIONAL ON-SITE STREAMS		
Reservoir evaporation	4.0	0.01
Ash disposal	22	0.06
Dust control	16	0.05
Sanitary and potable water	4.8	0.01
Service and fire water	9.6	0.03
Sewage returned	9.8	0.03
NET WATER USED		
(See Text)	1200	3.5

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*Includes sewage from satellite town.

TABLE 11-8. APPROXIMATE WATER REQUIREMENTS

Plant Hygas-SNG Site Wyoming

Plant size 250 x 10^6 scf/day ; 10.09 x 10^9 Btu/hr

(Note that all water rates are for on-stream times. In calculating annual average multiply by stream factor.)

	10^3 lb/hr	10^6 gal/day	gal/10^6 Btu product
PROCESS			
Boiler feed water into process	1,015	2.92	12.06
Foul water out of process	294	0.85	3.50
Clean water out of process	201	0.58	2.39
COOLING			
Water evaporated for cooling	279	0.81	3.32
FLUE GAS DESULFURIZATION	104	0.30	1.24
MINE AND OFF-SITE			
Road, mine and embankment dust control	13	0.04	0.15
Handling and crushing dust control	31	0.09	0.37
Sanitary and potable water	1.7	0.00	0.02
Service and fire water	2.6	0.01	0.03
Sewage returned*	303	0.87	3.60
Revegetation	0	0	0
ADDITIONAL ON-SITE STREAMS			
Reservoir evaporation	2.9	0.01	0.03
Ash disposal	86	0.25	1.02
Dust control	15	0.04	0.18
Sanitary and potable water	4.8	0.01	0.06
Service and fire water	9.6	0.03	0.11
Sewage returned	9.8	0.03	0.12
NET WATER USED			
(See Text)	851	2.5	10.1

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*Includes sewage from satellite town.

TABLE 11-9. APPROXIMATE WATER REQUIREMENTS

Plant Synthane-SNG Site Wyoming

Plant Size 250 x 10^6 scf/day ; 9.79 x 10^9 Btu/hr as gas

(Note that all water rates are for on-stream times. In calculating annual average multiply by stream factor.)

	10^3lb/hr	10^6gal/day	gal/10^6 Btu product
PROCESS			
Boiler feed water into process	1167	3.36	14.31
Foul water out of process	516	1.49	6.33
Medium quality water out of process	158	0.46	1.94
Clean water out of process	140	0.40	1.72
COOLING			
Water evaporated for cooling	299	0.86	3.66
FLUE GAS DESULFURIZATION	269	0.77	3.30
MINE AND OFF-SITE			
Road, mine and embankment dust control	16	0.05	0.20
Handling and crushing dust control	38	0.11	0.47
Sanitary and potable water	1.7	0.00	0.02
Service and fire water	2.6	0.01	0.03
Sewage returned*	303	0.88	3.72
Revegetation	0	0	0
ADDITIONAL ON-SITE STREAMS			
Reservoir evaporation	3.9	0.01	0.04
Ash disposal	55	0.16	0.67
Dust control	19	0.05	0.23
Sanitary and potable water	4.8	0.01	0.06
Service and fire water	9.6	0.03	0.11
Sewage returned	9.8	0.03	0.12
NET WATER USED (See Text)	860	2.5	10.5

---

*Includes sewage from satellite town.

TABLE 11-10. APPROXIMATE WATER REQUIREMENTS

Plant Solvent Refined Coal Site Wyoming

Plant Size 10,000 tons/day ; 13.34 x 10^9 Btu/hr

(Note that all water rates are for on-stream times. In calculating annual average multiply by stream factor.)

	10^3 lb/hr	10^6 gal/day	gal/10^6 Btu product
PROCESS			
Boiler feed water into process	715	2.06	6.43
Foul water out of process (1)	275	0.79	2.47
Water from gas purification	264	0.76	2.37
Water from gasification train	163	0.47	1.47
Clean water out of process	87	0.25	0.78
COOLING			
Water evaporated for cooling	229	0.66	2.06
FLUE GAS DESULFURIZATION	0		
MINE AND OFF-SITE			
Road, mine and embankment dust control	16	0.05	0.14
Handling and crushing dust control	39	0.11	0.35
Sanitary and potable water	1.7	0.00	0.02
Service and fire water	2.6	0.01	0.02
Sewage returned (2)	303	0.88	2.72
Revegetation	0	0	0
ADDITIONAL ON-SITE STREAMS			
Reservoir evaporation	2.9	0.01	0.03
Ash disposal	104	0.30	0.94
Dust control	19	0.05	0.17
Sanitary and potable water	4.8	0.01	0.04
Service and fire water	9.6	0.03	0.09
Sewage returned	9.8	0.03	0.09
NET WATER USED			
(See Text)	100	0.29	0.90

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(1) Section 7.4, not Table 7-1.

(2) Includes sewage from satellite town.

PART 2 - WATER TREATMENT

SECTION 14

WATER ANALYSES

This section begins the second part of the report, which is devoted to the quality and treatment of water. In this section are given the analyses of various key water streams in coal conversion plants supply waters, effluent waters that need treatment for reuse and waters influent to boilers. Circulating cooling water is also discussed.

Each subsection deals with a different water stream. The source water at each of the three sites is given on Tables 14-1 to 14-4 as follows:

Lake water for North Dakota site = Table 14-1
Brackish water for New Mexico site = Table 14-2
Sewage from satellite town for Wyoming site = Table 14-3
Additional river water for Wyoming site = Table 14-4

The two analyses assumed for foul process condensate are given in Table 14-5. These are composite pictures made from the few analyses that are available.

14.1 SOURCE WATERS

The effect of a brackish water and of municipal sewage as an intake has been investigated as part of this study. A different water is assumed at each site. In North Dakota the water will be drawn from Lake Sakakawea and have the analysis shown on Table 14-1. This is good quality water.

TABLE 14-1. ANALYSIS OF WATER FROM LAKE SAKAKAWEA, NORTH DAKOTA

	mg/l	mg/l (as $CaCO_3$)
Ca^{+2}	49	123
Mg^{+2}	19	78
Na^{+}	59	127
HCO_3^{-}	180	148
SO_4^{-2}	170	177
Cl^{-}	9	13
Silica	7	
Suspended solids	2	
Dissolved solids	420	

TABLE 14-2. ANALYSIS OF BRACKISH GROUNDWATER NEAR GALLUP, NEW MEXICO

	mg/l	mg/l (as $CaCO_3$)
Ca^{+2}	12	30
Mg^{+2}	13	53
Na^{+}	893	1941
CO_3^{-2}	45	75
HCO_3^{-}	408	335
SO_4^{-2}	509	529
Cl^{-}	770	1086
NO_3^{-}	1	1
F^{-}	2	5
SiO_2	5.6	
Suspended solids	10 (nominal)	
Dissolved solids	2660	

TABLE 14-3. ANALYSIS OF SEWAGE AT WYOMING SITE

	mg/l	mg/l (as $CaCO_3$)
Raw sewage		
BOD_5	250	
Suspended solids	300	
Total N	50	
Total P	12	
Treated sewage		
BOD_5	30	
COD	170	
Suspended solids	113	
Total N	20	
Total P	9	
Ca^{+2}	60	150
Mg^{+2}	25	103
Na^{+}	150	327
HCO_3^{-}	330	270
SO_4^{-2}	110	114
Cl^{-}	145	204
SiO_2	40	
Dissolved solids	830	

TABLE 14-4. ANALYSIS OF WATER FROM YELLOWSTONE RIVER NEAR HARDIN, MONTANA

	mg/l	mg/l (as $CaCO_3$)
Ca^{+2}	46	115
Mg^{+2}	16	66
Na^{+}	45	98
HCO_3^{-}	160	131
SO_4^{-2}	147	153
Cl^{-}	7	10
Silica	12	
Suspended solids	171	
Dissolved solids	364	

TABLE 14-5. EXEMPLARY ANALYSES OF FOUL WATER FROM SRC AND FROM GAS PLANTS

	Hygas and Lurgi Plants (mg/l)	Synthane and SRC Plants (mg/l)
BOD_5	13,000-18,700	about 30,000
COD	25,000-30,000	30,000-40,000
Phenol as C_6H_5OH	4,000-6,600	4,000-6,600
NH_3 as N	3,500-4,500	about 12,600*
HCO_3	about 13,000	about 4,000*
Sulfide as S	low	about 14,600*
Ca	about 20	about 20
Mg	about 15	about 15
Na	about 80	about 80
Cl	**	**
SO_4	low	low

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*These numbers apply to SRC only. In the Synthane water these components are taken to be the same as in the Hygas water.

** Chloride concentrations

	Wyoming	Navajo	North Dakota
Synthane	600		
Hygas	600	200	1200
SRC	600	200	1200
Lurgi	600	200	1200

Furthermore, water will be assumed to be available at about 30¢/thousand gallons at the site which is about 25 miles from the Lake.

In New Mexico the source water will be brackish groundwater having the composition shown on Table 14-2. This water will be pumped from a well and is assumed to cost 40¢/thousand gallons at the site.

In Wyoming some of the water will be sewage from a satellite town. The analyses of the treated and untreated sewage is given on Table 14-3. Untreated sewage is assumed to be free. Treated sewage costs about 67¢ per thousand gallons based on California experience.[1]

About 0.87×10^6 gallons/day is available from the satellite town. Additional water, having the composition shown on Table 14-4, is available from the Yellowstone River near Hardin, Montana; but this is assumed to be about 150 miles from the plant and water is expensive. Nonsewage water is taken to cost at least $1.80/thousand gallons on site.

14.2 FOUL PROCESS CONDENSATE

The water recovered directly from the coal conversion reactors is the dirtiest water in the plant. It is heavily contaminated with organic matter and ammonia. On the other hand, the metal content is probably low. (The chloride content may be high as is discussed below.) In the pilot plants the water quality is varying as the process conditions are varied for test purposes. It is not certain how much variation is expected in actual operation. The water quality depends on the process and on the coal. There is not enough knowledge about these waters for a really good design of a treatment plant. For the purposes of designing treatment two analyses have been considered: one for the Hygas and Lurgi plants and one for the SRC and Synthane plants; both are shown on Table 14-5. These analyses follow the reported analyses described below. It should not be assumed that Table 14-5 shows exact analyses of water from the named processes. As described below the exact analyses are not known. What is shown on Table 14-5 is a set of highly probable analyses for which it is valuable to study the water treatment. The various analyses will now be considered one at a time.

COD and Phenol

Some experimental analyses for gas plants using Western coals are given on Table 14-6. In Appendix 1 our analytical procedures are listed. Clearly, organic contamination is heavy, particularly phenol. There may be, however, much oxygen demand other than phenol present. Phenol has a theoretical oxygen demand of 2.38 (lb/lb) and this is close to the measured COD and BOD.[7] Thus for the two Synthane analyses shown on Table 14-6, phenol represents 33-41 percent of the COD. For the Lurgi analyses phenol represents 44-90 percent of the COD. The phenol in the coke oven water analysis given in Reference 2 is 68 percent of the COD. From the analyses of Central and Eastern coals given in Table 14-9, phenol represents 21-46 percent of the COD. Studies have been made to discover the nature of the organic contaminants in condensate from the Synthane process at the Bureau of Mines.[5] Oxygen-containing molecules predominate. "Fatty acids" regularly reported in analyses of Lurgi process water are not apparent in the results given. Fatty acids are determined on a sample steam distilled from acidified liquor by titration to a phenolphthalein end point.

Although the organic contamination is assumed the same in water from the Lurgi and Hygas processes, and the Synthane and SRC processes, this assumption is only a first approximation. Logic, borne out by conversations with pilot plant engineers, says that processes having higher temperatures at the top and longer residence times should give less organic contamination in the condensate water. Of the gasification processes the Lurgi and Synthane processes might be expected to give the dirtiest water and the Hygas process water to be notably cleaner. (Not all of the analyses shown here were available at the time the treatment plant designs were started. The phenol in Hygas water is probably less than that shown on Table 14-5, which is a guess.) The CO_2-Acceptor process, which has a fluid bed of long residence time, gives a relatively clean condensate. Water from the high temperature Koppers-Totzek process (discussed in the next section) is quite clean, and water from the Bigas process would be expected to be similarly clean.

The rank of coal must also be expected to affect the water. Analysis and experiment shows this to be true. Some analyses from Central and Eastern

TABLE 14-5. ANALYSIS OF FOUL PROCESS CONDENSATE, WESTERN COALS

(mg/l unless noted)

Process	Synthane	Synthane	Hygas	Hygas
Coal	Wyoming Subbit.	North Dakota Lignite	Montana Lignite	Montana Lignite
Ref. or note	2	2	8, f	8, g
pH (units)	8.7	8.7		
TDS				
TDS (after ignition)				
Total Carbon			7,800	6,414
Total Organic Carbon			5,270	3,936
Inorganic Carbon			2,630[f]	2,478[b]
Bicarbonate (HCO_3^-)			13,400[c]	12,600[c]
HCO_3^- (as meq/l)			219[c]	207[c]
BOD (5 days)			13,000	
BOD (15 days)			14,000	
BOD (20 days)			17,500	
COD	43,000	38,000	30,000[d]	13,590
Phenol as C_6H_5OH	6,000	6,600		
Fatty Acids as Acetic				
Total Ammonia as N			3,618	2,785[e]
Free Ammonia as N	9,520	7,200		
Total Ammonia (meq/l)				
Cyanide as CN	0.23	0.1	5.5	
Thiocyanate	23	22		
Total Sulfur as S			ND[a]	
Sulfide				
Chloride				

[a] ND = none detected

(continued)

(TABLE 14-6 continued)

(mg/l unless noted)

Process	Lurgi (ref. 3)			
Coal	Rosebud, Montana, Subbituminous			
	Coarse Graded Coal		Fine Graded Coal	
Note	h	i	h	i
pH (units)	9.6	8.3	9.5	9.8
TDS	4,030	1,765	10,540	1,650
TDS (after ignition)	45	35	60	25
Total Carbon				
Total Organic Carbon				
Inorganic Carbon	1,110[j]	5,307[j]	194[j]	4,284[j]
Bicarbonate (HCO_3^-)	5,642[p]	26,978[p]	982[p]	21,794[p]
HCO_3^- (as meq/l)	93[p]	442[p]	16[p]	357[p]
BOD (5 days)	9,900	13,400	9,100	5,200
BOD (15 days)				
BOD (20 days)				
COD	22,700	20,800	16,600	19,600
Phenol as C_6H_5OH	4,200	4,400	6,300	4,800
Fatty Acids as Acetic	1,250	1,670	1,780	550
Total Ammonia as N	4,385	14,540	1,720	14,380
Free Ammonia as N	3,990	14,015	1,180	13,990
Total Ammonia (meq/l)	258	855	101	840
Cyanide as CN	2	4	3	5
Thiocyanate	6	16	95	75
Total Sulfur as S	150	265	160	535
Sulfide	122	108	10	301
Chloride	45	40	80	30

(continued)

(TABLE 14-6 continued)

NOTES

a: Two samples, analyzed by Water Purification Associates.
b: Calculated as (Total Carbon)-(Organic Carbon) (see Appendix 1).
c: Calculated as equivalent to inorganic carbon.
d: Suspect value, high compared to total organic carbon; see Appendix 1.
e: Total Kjeldahl nitrogen = 2,800 mg/l.
f: Absorption spectrographic analysis gave
Ca 17
Mg 12
Na 115
g: Absorption spectrographic analysis gave
Ca 61
Mg 11
Na 84

Emission spectrograph gave

	result	relative scale
Calcium	high	>10
Sodium	low-medium	10^{-1} - 10
Magnesium	low-medium	10^{-1} - 10
Barium, Strontium	trace-low	10^{-2} - 10
Aluminum, Boron	trace	10^{-2} - 10^{-1}
Titanium	faint trace-trace	10^{-3} - 10^{-1}
Manganese, Iron, Zinc	faint trace	10^{-3} - 10^{-2}
Silicon, Vanadium	very faint trace	10^{-4} - 10^{-3}
Chromium, Silver, Tin, Copper	very very faint trace	$<10^{-4}$

h: Sample from inlet tar separator (labelled 1 in Ref. 3).
i: Sample from inlet oil separator (labelled 2 in Ref. 3).
j: Given as "carbonate as CO_2" in Ref. 3; converted to C for tabulation.

TABLE 14-7. CONTAMINANTS IN PRODUCT WATER FROM COAL GASIFICATION (HIGH-RESOLUTION MASS SPECTROMETER DATA) (REFERENCE 5)

Mass (nominal)	Precise mass, amu		[1]Δ × 10³	Formula	Possible compound type
	Obs.	Calc.			
79	79.044	79.042	2	C_5H_5N	Pyridine;
93	93.058	93.057	1	C_6H_7N	Methylpyridine;
94	94.041	94.042	1	C_6H_6O	Phenol;
107	107.071	107.074	3	C_7H_9N	C_2-pyridine;
108	108.055	108.057	2	C_7H_8O	Cresol;
110	110.036	110.037	1	$C_6H_6O_2$	Dihydroxybenzene;
117	117.057	117.058	1	C_8H_7N	Indole;
120	120.056	120.057	1	C_8H_8O	Acetophenone;
121	121.088	121.089	1	$C_8H_{11}N$	C_3-pyridine;
122	122.036	122.037	1	$C_7H_6O_2$	Benzoic acid, hydroxybenzaldehyde;
	122.073	122.073	0	$C_8H_{10}O$	C_2-phenol;
124	124.052	124.052	0	$C_7H_8O_2$	C_1-dihydroxybenzene;
129	129.055	129.058	3	C_9H_7N	Quinoline;
132	132.055	132.058	3	C_9H_8O	Indenol;
134	134.035	134.037	2	$C_8H_6O_2$	Hydroxybenzofuran;
	134.070	134.073	3	$C_9H_{10}O$	Indanol;
135	135.104	135.105	1	$C_9H_{13}N$	C_4-pyridine;
136	136.051	136.052	1	$C_8H_8O_2$	C_1-benzoic acid, methoxybenzaldehyde;
	136.087	136.088	1	$C_9H_{12}O$	C_3-phenol;
138	138.066	138.068	2	$C_8H_{10}O_2$	C_2-dihydroxybenzene;
143	143.072	143.073	1	$C_{10}H_9N$	Methylquinoline;
144	144.056	144.058	2	$C_{10}H_8O$	Naphthol;
146	146.069	146.073	4	$C_{10}H_{10}O$	C_1-indenol;
148	148.052	148.052	0	$C_9H_8O_2$	C_1-benzofuranol;
150	150.013	150.014	1	C_8H_6OS	Hydroxybenzothiophenol;
	150.069	150.068	1	$C_9H_{10}O_2$	C_2-benzoic acid, C_2-hydroxybenzaldehyde;
157	157.087	157.089	2	$C_{11}H_{11}N$	C_2-quinoline;
158	158.073	158.073	0	$C_{11}H_{10}O$	C_1-naphthol;
186	186.066	186.068	2	$C_{12}H_{10}O_2$	Biphenol;

[1] Difference between measured and calculated precise mass.

TABLE 14-8. CONTAMINANTS IN PRODUCT WATER FROM COAL LOW-VOLTAGE
MASS SPECTROMETER DATA, ppm BY WEIGHT (REFERENCE 5)

Promoter	Illinois No. 6 (bulk)										Montana (lump)			N. Dak. (lig)		Wyo. (bulk)	W. Va. (bulk)	Pgh. (bulk)
	None	None	2 pct limestone		2 pct quicklime	5 pct quicklime	Air instead of O_2	Coal fed directly into gasifier bed			None	Air instead of O_2		None	Air instead of O_2	None	None	None
			1	2				1	2	3		1	2					
Phenol	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
Cresols	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
C_2-phenols	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
C_3-phenols	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
Dihydrics	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	—	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
Benzofuranols	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
Indanols Acetophenones	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
Hydroxy-benzaldehyde Benzoic acids	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	—	—	—	[illegible]	—	[illegible]	[illegible]	[illegible]
Naphthols	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
Indenols	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
Benzofurans	—	—	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	—	—	—	[illegible]
Dibenzofurans	—	—	—	—	—	—	—	—	—	[illegible]	—	—	—	—	—	—	—	—
Biphenols	[illegible]	[illegible]	—	—	—	[illegible]	—	—	—	[illegible]	—	—	—	—	—	[illegible]	[illegible]	[illegible]
Benzothio-phenols	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	—	—	—	[illegible]	—	[illegible]	[illegible]	[illegible]
Pyridines	—	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
Quinolines	—	—	[illegible]	—	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	—	—	—	[illegible]
Indoles	—	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	—	[illegible]	[illegible]	[illegible]

TABLE 14-9. ANALYSIS OF FOUL PROCESS CONDENSATE, CENTRAL AND EASTERN COALS

(mg/l unless noted)

Process	Synthane	Synthane	Synthane	Hygas
Coal	Illinois No. 6	Western Kentucky	Pittsburg Seam	Illinois No. 6
Ref. or note	2	2	2	a
pH (units)	8.6	8.9	9.1	
Total Carbon				1225
Total Organic Carbon				702
Inorganic Carbon				523[c]
Bicarbonate (HCO_3^-)	11,000[b]			2,658[d]
HCO_3^- (as meq/l)	180			46
Carbonate	6,000[b]			
BOD (5 days)				2,652
BOD (20 days)				3,016
COD	15,000	19,000	19,000	4,000
Phenol as C_6H_5OH	2,600	3,700	3,700	273
Total Ammonia as N	8,100	10,000	11,000	7,200
Free Ammonia as N	6,890			
Total Ammonia (meq/l)	476	588	647	422
Cyanide as CN	0.6	0.5	0.6	
Thiocyanate	152	200	188	
Sulfur	e			f
Chloride				260

Notes

a. Analysis by Water Purification Associates.
b. Not from same analysis (footnote in Ref. 2)
c. By difference (see Appendix 1).
d. Calculated assuming equivalent to inorganic carbon.
e. $S^=$ 400
$SO_3^=$ (as S) 170
$SO_4^=$ (as S) 467
$S_2O_3^=$ (as S) 571
f. $SO_4^=$ (as S) 118

coals are presented on Table 14-9.

There is no reason to suppose that the analysis of water from oil producing processes (SRC, Synthoil, H-Coal) should be comparable to the analysis of water from oxygen blown gasifiers (Lurgi, Synthane). However, the analyses of SRC water given on Table 14-10 (for Kentucky coal) are quite similar to the Synthane water given on Table 14-6 (except for ammonia and sulfide contents), and when discussing biological treatment a single example has been used for SRC and Synthane.

Ammonia

Ammonia is a major contaminant in all the waters and it is derived from nitrogen in the coal. If, however, one tries to calculate the concentration of ammonia in the foul condensate on the assumption that all of the nitrogen in the feed coal ends up as ammonia in condensate, the concentrations found are 34,000-40,000 mg/l for Hygas, 30,000 mg/l for Synthane and 25,000-57,000 mg/l for SRC. In no process does even the major portion of the coal nitrogen end up as ammonia in condensate, but in SRC a much higher fraction goes this route than in gas processes. In the gas plants the calculations are clearly dependent not only on the quantity of nitrogen in the coal but on the conditions chosen which determine the quantity of condensate as well. At high temperatures, as in the Koppers-Totzek process, ammonia is not formed and free nitrogen is released. The appearance of free nitrogen cannot be verified in the Hygas pilot plant because all line purging is done with nitrogen.

Sulfur

Sulfur in coal can be expected to be mostly converted to H_2S. Although carbon dioxide, present in large amounts in gas plants, is a stronger acid than hydrogen sulfide, equilibrium is not reached and some hydrogen sulfide is found in condensate. In Western coals, where the sulfur content is low, the sulfide content of the water is low and has been ignored in the design of the ammonia separation equipment. H_2S is more volatile than CO_2 and will be stripped out and removed with the CO_2. In the SRC plant CO_2 is not

TABLE 14-10. ANALYSIS OF FOUL PROCESS CONDENSATE, SOLVENT REFINED COAL

(mg/l unless noted)

Process	Solvent Refined Coal	
Coal	Kentucky	
Ref. or note	a	
pH (Units)	8.6	9.2
Total Carbon	9,000	8,160
Total Organic Carbon	6,600	7,390
Inorganic Carbon	2,400[b]	770[b]
BOD (5 days)	32,500	
BOD (15 days)	34,500	
BOD (20 days)	>34,500	
COD	41,600	25,000-31,000
Phenol as C_6H_5OH	5,000	12,000
Total Kjeldahl N	8,300[c]	15,000[c]
Total Ammonia as N	7,900	14,000
Total Ammonia (meq/l)	465	14,000
Cyanide as CN	10	
Total Sulfur as S	10,500[c]	16,200[c]
Ca	0.47	
Mg	0.13	
Si	<0.5	

Notes

a: Analysis by Water Purification Associates and Pittsburg and Midway.

b: By difference, see Appendix 1.

c: 22 analyses for N and S made between 11/5/75 and 12/9/75 were supplied by Pittsburg and Midway. Four of these analyses had extreme values and were arbitrarily eliminated. For the remaining 18 analyses the average total nitrogen was 12,600 mg/l with a standard deviation of 7,000 mg/l which is very random. The average ratio (moles NH_3)/(moles H_2S) was 2.0 with a standard deviation of 0.17 which is quite reproducible.

present in large amounts and H_2S is found in the water, associated with ammonia.

Alkalinity

The bicarbonate shown on Table 14-1 for gas plants is not the result of analysis. It is calculated as 0.75 moles CO_2 per mole NH_3 and is about as much CO_2 as can be expected judging from vapor pressure data given in Section 15.

Chloride

Chloride is of interest particularly if condensate is to be treated to boiler feed quality. Chlorine in coal mineral is converted to HCl by the conversion process.[8,9] The chloride material balances on the Synthane PDU gasifier reported in Reference 6 do not balance, but they do show that condensate is the only important way in which chlorine left the plant. Three tests were done using Illinois No. 6 coals:

wt % Cl in coal	mg/l Cl in condensate
0.0091	300
0.0220	170
0.0093	190

The concentration in condensate is comparable to the value found for Hygas using Illinois No. 6 (Table 14-9). The ratio of condensate to coal in these tests is more than twice the ratio found in the material balance of Section 6.

The chlorine content of coals is not always given. It lies in the range zero to 0.5 wt percent with zero often being found.[10] We have no suggested value for Navajo coal. For Wyoming coal 0.04 wt percent (dry basis) has been reported in one case[11] and for North Dakota lignite 0.2 wt percent (dry basis) has been reported.[12] If all the chlorine in the coal ended up as chloride in condensate, then material balances would give

		Cl concentration (mg/l)
Synthane:	Wyoming	1,200
Hygas:	Wyoming	1,400
	North Dakota	8,000
SRC:	Wyoming	3,000
	North Dakota	13,000
Lurgi:	Wyoming	600
	North Dakota	2,000

These are high concentrations. The calculation depends as much on the condensate rate (which depends on chosen process conditions and whether dry or wet coal is used) as it does on the chlorine content of coal. Neither of these numbers is well known. Wide variations in chloride concentration of condensate are to be expected from coal to coal and from design to design. The numbers shown on Table 14-5 are illustrative only. The chloride can prevent distillation of ammonia. For biological treatment 450 mg/l nitrogen should be left in the water as nutrient. Chloride equivalent to this much nitrogen has a concentration of 1,100 mg/l, so fixed ammonia may not be troublesome.

Table 14-11 shows the concentrations in condensate of a wide variety of elements when using Illinois No. 6 coal in a Synthane gasifier. Additional analyses of metals are given in notes *f* and *g* of Table 14-9 for the Hygas process using Montana lignite, and on Table 14-10 for SRC using Kentucky coal. The analyses are too few to be sure, but there seems to be a difference between Montana lignite on one hand and between Illinois and Kentucky coal on the other hand. There also seems to be no large concentration in any case. The metal concentrations on Table 14-5 are approximate.

The analyses presented in Table 14-5 will be used for the design of the water treatment plants.

TABLE 14-11. TRACE ELEMENTS IN CONDENSATE FROM AN ILLINOIS NO. 6 COAL SYNTHANE GASIFICATION TEST

From Reference 2

	No. 1	No. 2	Average (by weight)
Ppm:			
Calcium	4.4	3.6	4
Iron	2.6	2.4	3
Magnesium	1.5	1.8	2
Aluminum	0.8	0.7	0.8
Ppb:			
Selenium	401	321	360
Potassium	117	104	160
Barium	109	155	130
Phosphorus	82	92	90
Zinc	44	81	60
Manganese	36	38	40
Germanium	32	61	40
Arsenic	44	28	30
Nickel	21	14	20
Strontium	33	24	30
Tin	21	26	20
Copper	16	20	20
Columbium	7	5	6
Chromium	4	8	6
Vanadium	4	2	3
Cobalt	1	3	2

Run No.*	162	163	164
Ppm			
S	5,000	5,000	5,000
Total carbon	16,000	16,000	16,000
B	41	1717 82	82
Cl	300	170	190
F	39	37	12
Na	6.6	6.0	5.4
Si	2.8	4.7	6.6

---

*From Reference 4. (Analyses by spark source mass spectrometer. Only S & C have satisfactory material balances around the system.)

14.3 CLEAN AND INTERMEDIATE PROCESS WATER

In addition to foul condensate the Hygas, Synthane and SRC plants have other water effluent streams. A stream that has been labeled clean condensate is obtained either from the water of reaction in methanation, or surplus water from the reverse of this reaction, namely, reforming in the SRC plant. This water is very clean as it comes from very clean conditions. A sample of methanation water is crystal clear and has no odor. Clean condensate will be saturated with CO_2, CO, CH_4 and H_2, but as it is always recovered hot and under pressure these gases will be assumed to be removed by flashing. After flashing, clear condensate is assumed to have less than 200 mg/l dissolved solids and to be suitable as boiler feed. The Hygas process has no other stream.

Condensate is recovered from two other points in the Synthane plant: after shift conversion and after acid gas removal. These streams will be mixed to give medium quality condensate. Since most of the condensable and water soluble contaminants in the gasifier off-gas appear in the foul condensate, and as no analyses of these downstream condensates are available, medium quality condensate is taken to have one tenth of the concentrations shown for foul condensate on Table 14-5.

In the Solvent Refined Coal plant condensate is obtained in the production of hydrogen by gasifying residue in Koppers-Totzek gasifiers. Because of the high temperature, condensate from the Koppers-Totzek process is quite clean. Table 14-12 shows a particular analysis of condensate water after it has been used to quench slag. Table 14-12 will be used for the SRC plants in this study.

Also in the SRC plant live steam stripping is used in Selexol type acid gas removal sections. There is a small acid gas removal plant for gas made in the dissolving section, but over 90 percent of the acid gas removal occurs in the reforming section where the gas is very clean, and in the Koppers-Totzek section where the gas is quite clean. Condensed stripping steam will contain carbon dioxide and H_2S which must be flashed, but there is no reason to expect much organic matter, ammonia or salts. We have chosen to use the approximate analysis of Table 14-13.

TABLE 14-12. ANALYSIS OF WATER FROM KOPPERS COAL GASIFICATION, KUTAHYA, TURKEY[a]

pH	8.9
	mg/l
Ca^{+2}	159
Mg^{+2}	68
Na^{+}	18
NH_4^{+}	122
Cl^{-}	46
$SO_4^{=}$	109
H_2S	Not detected
COD	61
Silica	43

TABLE 14-13. EXEMPLARY ANALYSIS OF CONDENSED STRIPPING STEAM FROM ACID GAS REMOVAL IN THE SRC PLANT

	mg/l
Ca^{+2}	20
Mg^{+2}	15
Na^{+}	18
Cl^{-}	40
$SO_4^{=}$	10
$CO_3^{=}$	50
COD	30
Silica	2

TABLE 14-14. SUGGESTED TOLERANCES IN BOILER WATER

Pressure (psig)	Total Dissolved Solids (mg/l)	Alkalinity (mg/l as $CaCO_3$)	Total Hardness (mg/l as $CaCO_3$)	Silica mg/l
Blowdown Concentrations				
300-450	3000	600	60	40 to 50
1000-1500	1000	200	0	2 to 5
Make-up Concentrations for 5% Blowdown				
300-450	150	30	0.3	2 to 2.5
1000-1500	50	10	0	0.1 to 0.25

14.4 BOILER FEED WATER

Table 14-14 is a partial listing of acceptable concentrations in boiler feed water modified from Reference 13. We will use Table 14-14. In the Hygas and Synthane plants boiler feed water must be prepared to 1000 psig quality. In the SRC plant 400 psig quality will suffice, as it will for most of the makeup boiler feed water in the power plants. In the power plants the makeup goes to the low pressure Lurgi gasifiers. The small amount of water needed as makeup to high pressure steam used for the electricity generation will require an extra deionization step.

14.5 COOLING WATER

A wet cooling tower is an evaporator, and salts dissolved in the makeup water will be concentrated, often to the point of precipitation. The precipitate, which usually consists of carbonates, sulfates and phosphates of calcium and magnesium together with silica, tends to adhere to heat transfer surfaces forming a hard scale and lowering the heat transfer coefficient. This must be prevented.

Not only may the makeup water contain silt but the circulating water, in its passage through the tower, scrubs dust out of the air. Circulating water thus contains an ever-increasing amount of suspended matter which will settle out in stagnant spots in the pipes and heat exchangers. This must also be prevented.

Circulating cooling water is warm and well oxygenated. It is seldom sterile when fed to the system and, in any case, receives a steady supply of air-borne growth. Untreated cooling systems will be subject to fungal rot of the wooden parts of the tower, bacterial corrosion of iron and bacterial production of sulfides and large growths of algae in the sunlit portions of the tower.[14] Biocidal chemicals must be added to control growth.

Finally, the well oxygenated circulating water can be very corrosive to heat transfer surfaces.

Treatment of cooling water is intended to prevent the problems of scaling, fouling, microbial growth and corrosion. In applying various treatments it is necessary to [illegible] the upper permissible limits of concentration of various dissolved substances so that the treatment procedures can be sized correctly.

Crits and Glover[15] have published a detailed set of recommendations which has been copied onto Table 14-15 together with the limits used in this study.

(a) Suspended solids. We have used a medium figure from Crits and Glover's recommendations.

(b) Calcium carbonate and bicarbonate ion. Because of the equilibrium

$$H^+ + CO_3^= \rightleftharpoons HCO_3^-$$

the concentration of $CO_3^=$ in solution depends on the concentration of H^+, that is, on the pH. The solubility of $CaCO_3$ depends, therefore, on pH as well as on temperature and the presence of other dissolved ions which affect the ionic strength of the solution. A procedure for calculating equilibrium solubility has been given by Langelier[16] and discussed by Larson and Buswell.[17] Sisson[18] and Sussman[19] have published nomograms based on Langelier's equation. Table 14-16 presents some solubilities calculated by Langelier's procedure at 122°F (50°C) and 800 ppm total dissolved solids.

It must be emphasized that Table 14-16 gives equilibrium solubilities.

TABLE 14-15. CONTROL LIMITS FOR COOLING TOWER CIRCULATING WATER COMPOSITION

	Conventional at low pH*	Suggested at high pH with high concentration and dispersants*	Used in this study
pH	6.5 to 7.5	7.5 to 8.5	
Suspended Solids (mg/l)	200 - 400	300 - 400	300
Ca x CO_3 (as $CaCO_3$)	1,200	6,000**	6,000
Carbonates (mg/l)	5	5	5
Bicarbonates (mg/l)	50 - 150	300 - 400	300
Silica (mg/l)	150	150 - 200	150
Mg x SiO_2 (mg/l)	35,000	60,000	60,000
Ca x SO_4 (as $CaCO_3$)	1.5×10^6 to 2.5×10^6	2.5×10^6 to 8×10^6	2.5×10^6
PO_4	---	---	20
Chlorides	---	---	3,000
NH_3 (mg/l)	---	---	20

---

* From Ref. 15

** More data needed to confirm (footnote from Ref. 15).

TABLE 14-16. SOLUBILITY OF $CaCO_3$ AT 50°C AND 800 ppm TDS CALCULATED FROM REF. 16

pH	Solubility Product*	Solubility** with equal concentrations of Ca and Alkalinity
6	830,000	911
6.5	262,500	512
7	83,000	288
8	8,300	91
9	830	29
10	83	9.1

---

* (Concentration Ca as ppm $CaCO_3$) x (Alkalinity as ppm $CaCO_3$).

** This is the square root of the solubility product.

In fact, as is pointed out by Feitler,[20] $CaCO_3$ will not form scale when it is present at many times its equilibrium solubility. Calcium carbonate easily supersaturates, and when precipitation does occur it is usually as a multitude of very fine crystals which do not grow and which remain in suspension. Furthermore, the lower the pH the lower the tendency to form scale. Figure 14-1 has been recalculated from Feitler.[20] The critical pH curve for scale formation was experimentally determined by Feitler for Los Angeles city water and, as he points out, is not totally representative of other waters.

The upper limit of the Crits and Glover recommendation for the calcium and carbonate solubility product has been used.

When air is passed through water containing bicarbonate, some carbon dioxide is evolved converting the bicarbonate to carbonate. For a bicarbonate limit a medium value from Crits and Glover has been used.

(c) Silica. The recommendation of Crits and Glover for the silica concentration (which is substantiated by Griffin[21] from experience in the power industry) has been used. Silica is removed from solution by coprecipitation with magnesia. The Crits and Glover recommendation for the solubility product $Mg \times SiO_2$ has been used.

(d) Calcium sulfate. A detailed review of the solubility of calcium sulfate has been given by Glater.[22] Two of the most complete studies are those of Marshall and Slusher[23] who studied the solubility in seawater concentrates at temperatures to 200°C, and Denman[24] who studied the solubility in cooling water. These authors give detailed procedures for calculating solubility. The solubility of calcium sulfate depends not only on temperature but on the concentration of other ions present. In pure water, calcium sulfate has a solubility of about 2100 mg/l as $CaCO_3$,[21] giving a solubility product of 2.4×10^6 as $(mg/l\ CaCO_3)^2$. According to Denman[24] the solubility of calcium sulfate in 5000 mg/l NaCl is about 2800 mg/l giving a solubility product of 4.4×10^6 as $(mg/l\ CaCO_3)^2$. A conservative solubility product of 2.5×10^6 as $(mg/l\ CaCO_3)^2$ has been chosen.

The Solubility of Calcium Phosphate

Ortho-phosphate scaling can be troublesome if phosphate is present.

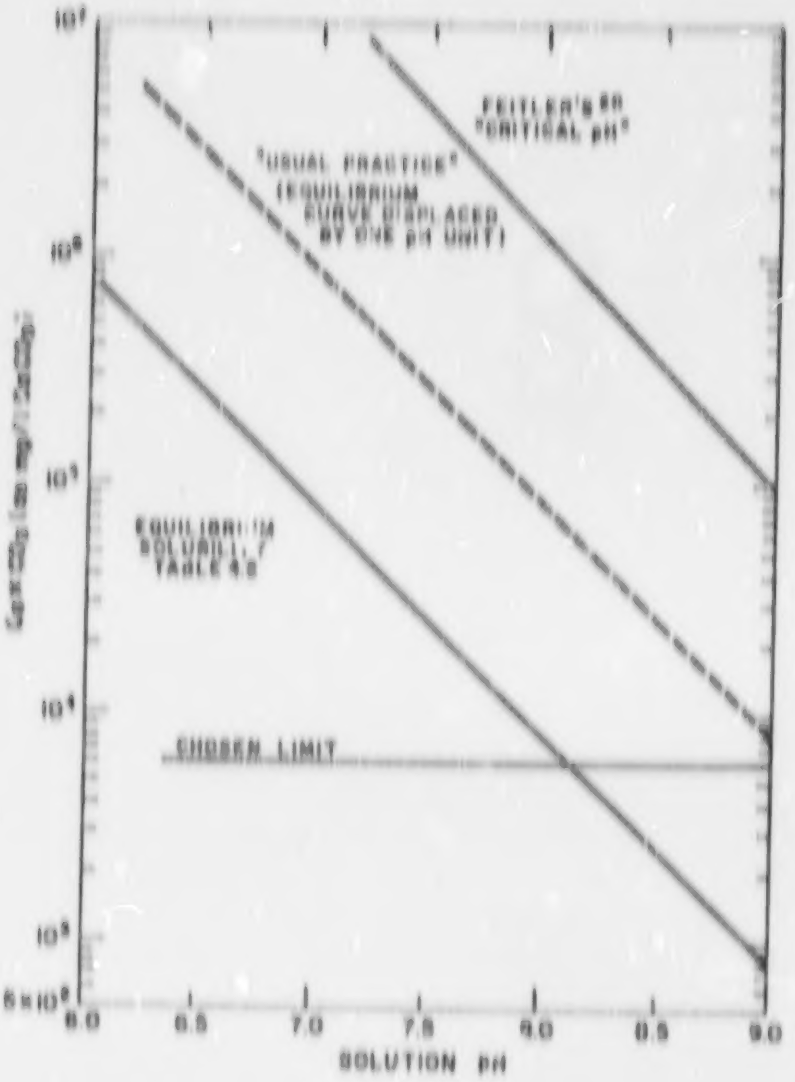

Figure 14-1. Scaling by calcium carbonate
(taken from Reference 20)

Phosphate will be present if sewage plant effluent is used as makeup. Phosphorus and nitrogen must be present as nutrients in biotreatment. Phosphate is added and ammonia is controlled by not stripping all of the ammonia out of process condensate. The feed waters to the biotreatment plants contain about 450 mg/l ammonia and 90 mg/l P (about 270 mg/l PO_4). When biotreatment is running smoothly (which cannot be guaranteed) it should be possible to reduce the feed concentrations of N and P to 5 percent without lessening the carbon conversion. In this study that biotreated foul condensate has been assumed to contain about 20 mg/l ammonia and 15 mg/l PO_4. The degree of nutrient makeup in the biological treatment seems not to have received such study, but it is important if biologically treated foul condensate is to be used as cooling tower makeup.

The salts, $Ca_3(PO_4)_2$, calcium ortho-phosphate and $Ca_5(OH)(PO_4)_3$, hydroxyapatite, are the least soluble form. The salts $CaHPO_4$ and CaH_2PO_4 are much more soluble. Precipitation of calcium phosphate depends therefore on pH. Details have been presented by McCoy[14] and Table 14-17 is taken from this reference. McCoy points out that precipitation can be slow and is complicated by complexes of calcium with other phosphates. In fact, much higher concentrations than suggested by Table 14-17 are used. Kluesner and others[26] found that a water containing 70 mg/l Ca as $CaCO_3$ and 0.5 mg/l ortho-phosphate as P (1.5 mg/l as PO_4) can be con[illegible]ted 15 times. The pH of the sewage was 7.5. Harpel[27] reports many successful uses of wastewater in cooling towers. The organic matter in the waste, particularly in treated sewage, stabilizes calcium phosphate. Concentrations of 30-50 mg/l ortho-phosphate have been successfully used. Phosphates, if stabilized, are usual corrosion inhibitors.[28] The limit given on Table 14-15 is arbitrary but seems to be quite safe according to References 21, 27 and 28.

Phosphate is a nutrient and its presence will encourage yeast and fungus growth. When phosphate is present biocide dosage will have to be increased.[27,29]

Chloride Limitations

At some point the concentration of chloride in the circulating water

TABLE 14-17. CALCIUM PHOSPHATE CONCENTRATIONS AT VARIOUS pH VALUES (TAKEN FROM REFERENCE 14)

	Maximum Ca (ppm as $CaCO_3$) at equilibrium				
ppm O-PO_4	pH = 5.0	pH = 6.0	pH = 6.5	pH = 7.0	pH = 7.5
10	1.59 x 10^4	700	175	49	12
25	8.97 x 10^4	379	94	26	6.5
50	5.66 x 10^3	240	59	16	4.0
75	4.30 x 10^3	182	45	13	3.2
100	3.72 x 10^3	151	37	11	2.7

limits further concentration. There are two limits to chloride concentration. The first is the corrosive effect on steel even with inhibitors present. It has been suggested that a chloride concentration of 3000 mg/l should not be exceeded[15] when using stainless steel. The second limitation on chloride is quite indefinite. Although very small, some drift will leave the tower and settle on adjacent foliage. If the spray is salty and rainfall to wash the leaves is limited, then plants can be damaged. For this study 3000 mg/l chloride has been arbitrarily taken as the upper permissible limit regardless of the material of the heat exchanger. Reference 25 indicates that for this concentration the maximum salt deposition rate is approximately 25 lbs/acre-yr at about 1½ miles from the tower and drops to 10 lbs/acre-yr at 3 miles and to 1 lb/acre-yr at 5 miles. This should be compared to the natural salt deposition rate of approximately 100 lbs/acre-yr at 5 miles from the ocean and 15 lbs/acre-yr at 35 miles inland.

Ammonia

All experience with treated sewage tower makeup includes experience with ammonia.[27,29,30] The problems have been summarized by Fleishman[30] and are: corrosion of copper, inactivation of zinc corrosion inhibitors, chlorine consumption and nutrient for biological growth. The concentration of NH_3 in the circulating water does not increase over its makeup water value. Air stripping and biological oxidation maintain the NH_3 concentration slightly higher than in the makeup water.[30] In this study copper is not used. Also, when ammonia is present quite high values of organic carbon are expected at the same time, so the use of oxidising biocides is not planned. Table 14-15 shows a somewhat high allowable concentration of ammonia, and if this concentration is present increased biocide usage will be required.

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SECTION 15

WATER TREATMENT TECHNOLOGIES

15.1 INTRODUCTION

In this section are given brief descriptions of water treatment technologies not described elsewhere. The subsections are the names of the technologies. Not all possible technologies are included in this section. If a particular technology is used in the overall plant design, then it is discussed. A few technologies are discussed even though they were not used in the plant designs. Wet oxidation was investigated quite thoroughly; it worked well but is too expensive compared to biological treatment at the organic loading of a typical [illegible] process condensate. The use of oxygen instead of air was not investigated, and this study is not the last word. Freezing is a treatment technology potentially extremely useful for obtaining water purified of inorganic and organic contamination simultaneously. Freezing is not developed and has never been tried on waters of the type of process condensate. Freezing is described here because of its future potential.

In this section a technology is discussed to arrive at its utility and cost. Design information, to which the study does not contribute, will be found in the references given.

15.2 WET OXIDATION

This is a procedure for the destruction of organic matter dissolved or suspended in water by oxidizing with air at high temperatures. The temperatures used are above the normal boiling point of water (212°F) and the reaction is carried out under pressure to prevent boiling. The pressure is usually 600 psig or above. Description and details will be found in Reference 1 and other references given therein.

The degree of oxidation achieved depends on the temperature and the material oxidized. A sample of water from the Hygas pilot plant was tested by Zimpro, Inc. in Rothschild, Wisconsin with the results shown on Table 15-1. It is apparent that satisfactory results were obtained. At 260°C with catalyst the COD was reduced by 93 percent and all the phenol removed.

Wet oxidation is a chemical oxidation by O_2 and the material destroyed does not have to be biodegradable. Wet oxidation will therefore be particularly useful when the waste is toxic, when the COD/BOD ratio is high and when the concentration is high. The cost of wet oxidation is not greatly dependent on the concentration of the feed water and the process works well on concentrated waters. This is quite different from biological oxidation. Costs estimated for various throughputs in the range 1.5×10^4 to 6×10^6 gal/day suggest that the capital cost can be estimated by[1]

$$\text{cost } (\$) = 650 \text{ (gallons/day)}^{0.7}$$

If 17 percent/yr of capital is charged for amortization and maintenance, this formula gives

Throughput (10^6 gallons/day)	Amortization Charges ($/thousand gallons)
0.5	7.20
1.5	5.20
3.0	4.20

The energy requirement for air compression is about 0.1 kw-hr/lb COD removed which is not high compared to biotreatment. However, the capital cost is high. The capital cost does not depend on the COD concentration and wet oxidation is particularly useful for very high COD (about 5 percent or more). Wet oxidation has not been used in this study.

TABLE 15-1. ANALYSES - HYGAS WASTEWATER WET OXIDATIONS

Sample	Feed	69A-36-1	69A-55-1	69A-58-1
Temp., °C	13.7	240	280	280
Time, Min.	---	60	60	60
COD, g/l	13.7	4.9	3.3	1.0
% COD Reduction	---	64.2	75.9	92.7
Total Solids, g/l	1.75	1.36	1.16	2.46
Total Ash, g/l	0.36	0.34	0.37	.38
pH	8.2	8.2	8.1	8.0
NH_3 as N, g/l	3.25	2.84	2.88	3.07
TKN, g/l	3.25	3.64	3.01	3.29
Total S, g/l	0.17	0.13	0.17	0.43
Total Halides as Cl, g/l	0.1	0.1	0.1	0.1
CO_2	10.4	5.8	6.2	7.2
Phenol, mg/l	740	<1.0	<1.0	<1.0
Cyanide, mg/l	0	0	0	0
Thiocynate, mg/l	0	0	0	0
BOD_5, mg/l	---	2,350	190	---
Catalyst	---	No	No	Yes

15.3 GRANULAR ACTIVATED CARBON ADSORPTION

Adsorption of the organic matter remaining in biologically treated condensate is one possible procedure for reducing the COD if treated condensate is to be fed to a boiler. The procedure is expensive and will probably not be used if the reuse of condensate is for anything other than boiler feed. It is not known to what level soluble COD can be reduced by carbon adsorption, but it may not be good enough for boiler feed and some oxidative treatment may have to follow the carbon.

Adsorption with granular activated carbon is a well-known procedure which will not be described here. Selected information, together with current quoted costs of carbon, have been used to estimate the cost of treatment as follows. Because of the very high COD of the feed water, a longer contact time than usual has been assumed in municipal plants as has the use of "pulsed" contactors which approach counter-current flow. The costs estimated more nearly approach those common to sugar refineries than those common to municipal treatments. Thermal regeneration is used and no contribution is planned from biological regeneration, so long on-stream times for the carbon are not required.

First, the secondary clarifiers in the biological treatment have been costed without addition of flocculating agent and without filtration of the overflow. This is satisfactory if the treated water is used as makeup to the cooling water because side stream clarification of circulating cooling water will be practiced. If biologically treated water is to go to carbon adsorption, then synthetic polymeric flocculants will be added to the clarifier (at 5 mg/l) and the overflow will pass through some form of automatic backwash sand filter.

If Q is the feed flow in gallons/minute, the capital cost of the filter is \$175Q. This will be amortized at 15%/yr with an additional 2%/yr for maintenance. The filter charge is

$$(0.17 \times 175Q\ \$/\text{yr}) \times (1\ \text{yr}/4.32 \times 10^5\ \text{mins})$$

$$\times\ (10^3/Q,\ \text{mins, thousand gallons})\ =\ \$0.07/\text{thousand gallons}$$

(This and all the other costs are summarized on Table 15-2.) Because all the charges are proportional to flow, they are expressed in $/thousand gallons.

The charge for the flocculating agent is

$$(\$1.60/\text{lb flocculant}) \times (5\ \text{lb flocculant}/10^{6}\ \text{lb water})$$

$$\times\ (8330\ \text{lb water/thousand gallons}) = \$0.07/\text{thousand gallons}$$

The carbon contactors are assumed to have an open vessel residence time of 120 minutes with an extra 120 minutes installed. Makeup carbon costs \$0.4/lb or, at 35 lb/ft^3, \$14/ft^3. When considering installing contactors, piping, valving, etc., \$10 has been added to the cost of one cubic foot of carbon. This will allow for vessels nearly twice the volume of the carbon that they contain. Thus installed carbon costs \$24/ft^3 or \$0.686/lb. In

TABLE 15-2. SUMMARY OF COSTS OF CARBON ADSORPTION

Q = flow (gallons/min)
s = COD removal (mg/l)
k = capital cost of regenerating
    furnace ($/lb carbon/day)

	Capital ($)	Expenses ($/thousand gallons)
Flocculation		0.07
Prefiltration	175Q	0.07
Contactors and Carbon	995Q	0.44
Regeneration Furnace	0.03Qsk	$1.5 \times 10^{-5}sk$
Fuel for Regeneration		$1.7 \times 10^{-4}s$
Pumping energy		0.001
Replacement Carbon		$4.6 \times 10^{-4}s$
	1170Q + 0.03Qsk	$0.58 + 6.3 \times 10^{-4}s$ $+ 1.5 \times 10^{-5}sk$

addition to the carbon in the contactors, an additional 120 minutes of carbon at makeup carbon price is in the regenerator and piping. The capital cost of contactors and carbon is

$$(Q/7.48,\ ft^3/min) \times (240\ mins) \times (24\$/ft^3) + (Q/7.48,\ ft^3/min)$$

$$\times\ (120\ mins) \times (14\$/ft^3)\ =\ \$995Q$$

The operating charges are taken at 15%/yr amortization plus 4%/yr maintenance which is $0.44/thousand gallons.

The cost of field-erected regenerating furnaces has been given in Reference 4 and can conveniently be expressed as

Capacity (lb carbon/day)	Installed cost [$/(lb carbon/day)]
less than 7,000	54
7,000 to 70,000	$8930/(capacity)^{0.577}$
more than 70,000	14.3

Regeneration begins at 0.4 lb COD/lb carbon. This is lower than might be obtained if biological regeneration occurred[3] but higher than recently reported refinery experience.[5] This somewhat high removal is justified because of the high COD in the feed water and because a counter-current system is used. The pounds of carbon regenerated per day are (where x is the COD in mg/l)

$$(8.33Q,\ lb\ water/min) \times (x/10^6,\ lb\ COD/lb\ water)$$

$$\times\ (1/0.4,\ lb\ carbon/lb\ COD) \times (1440,\ min/day)\ =\ 0.03\ Qx\ lb\ carbon/day$$

If k is written for the capital cost in $/(lb carbon/day) then the capital cost of the regenerating furnace is $0.03 Qxk.

The charges for regeneration are taken as 15%/yr for amortization plus another 7% for maintenance and are therefore $1.5 \times 10^{-5}xk$ $/thousand gallons.

The assumed opened vessel capacity of 240 minutes means that 1120Q lb carbon are installed. The regeneration rate is 0.03yx lb/day, so the number of days that the carbon is on line between regenerations is $3.7 \times 10^4/x$. If $x = 10,000$ mg/l, this means 3.7 days between regenerations which seems adequate.

The energy for regeneration is about 4,500 Btu/lb carbon, divided between fuel and steam, and is taken to cost $1.00/$10^6$ Btu, or
$1.69 \times 10^{-4}x$ $/thousand gallons.

The pumping energy is enough to lift the flow through about 15 psi. (With a linear velocity of 5 gpm/ft^2, a 120 minute contact time means 80 ft total for the carbon. The pressure drop is assumed to be 2 inches water per foot of carbon and 7 psi is added for other pressure drops.) At 2¢/kw-hr this costs $0.003/thousand gallons.

Replacement carbon is 5.5 percent of the regenerated carbon and costs $4.58 \times 10^{-4}x$ $/thousand gallons.

In keeping with the other cost estimates, labor and laboratory charges are ignored. Some costs are shown on Figure 15-1. The effect of throughput on $/thousand gallons is not significant. Above about 3,000 mg/l COD removed, the costs become very high. Carbon adsorption is only suitable for low concentrations. The assumed carbon loading gives an energy requirement for regeneration of about 11,000 Btu/lb COD removed. This energy might make about 1.1 kw-hr of electricity and is about twice the energy needed to remove 1 lb BOD in an activated sludge plant. The energy is 93.7x (Btu/thousand gallons) and is

COD removed (mg/l)	Energy for carbon regeneration (10^6 Btu/thousand gallons)
3,000	0.3
10,000	0.9

For high removal rates figure 15-1 tends to a cost of 11¢/lb COD removed. This can be compared with the cost of biotreatment of 2.1¢/lb BOD removed. There is very little published experience on the use of carbon for coke plant wastes. VanStone[36] presents an adsorption isotherm and a cost estimate made in 1972. Costs tend to 8¢ to 9¢/lb phenol removed, which is

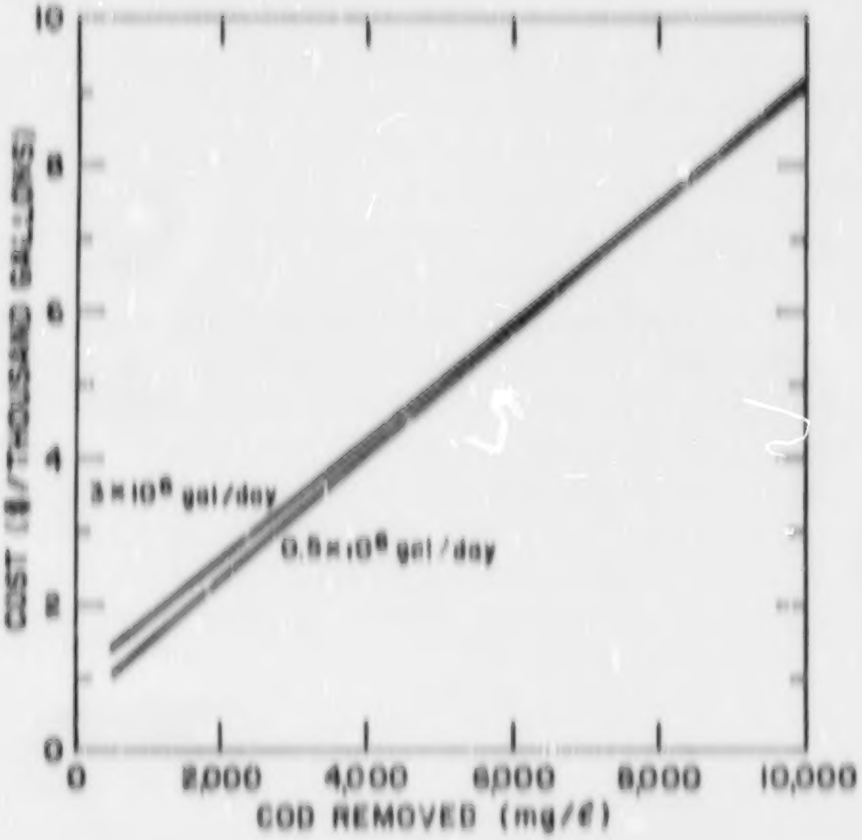


Figure 15-1. Costs of granular activated carbon adsorption.

about 4¢/lb COD removed. This is low. VanStone uses lower unit costs than here, but the most important difference is the use of a carbon loading of about 0.3 lb soluble organic carbon/lb carbon, or about 1 lb COD/lb carbon.

Other Adsorption Possibilities

Wet oxidation, described in Section 15.1, has been investigated for the regeneration of powdered activated carbon.[7] It has proved satisfactory. If this procedure is used to replace granular activated carbon, the cost of contractors is much reduced. The furnace is not required and the fuel is reduced. The replacement carbon is not much altered and the cost of the wet oxidation reactor must be added. This replacement does not seem worthwhile unless the COD removed is more than about 8,000 mg/l.

The possibility of selective adsorption of phenol on a synthetic polymeric adsorbent is discussed in Section 17. The general use of synthetic polymeric adsorbents is not included in this study.

Synthane char is being studied as an absorbent at the Bureau of Mines.

15.4 FREEZING

When dirty water is frozen the ice crystals formed tend to exclude contaminants and to be very pure water. A practical consideration is that it is much easier if the fraction of water recovered as ice is low enough to leave all of the original contaminants in solution in the unrecovered water. Contaminants should not precipitate. With foul process condensate water, about 90 percent of the water might be recoverable. An advantage of freezing is that all sorts of contaminant molecules are excluded, organic as well as inorganic, ionized and unionized. The energy consumption is expected to be less than 70 kw-hr/thousand gallons in direct contact freezing; this is equivalent to 0.7×10^6 Btu/thousand gallons assuming 10,000 Btu/kw-hr to generate electricity.[1]

However, no large-scale freezing unit is available nor have tests ever been made on these waters. Freezing is not used in this study, but laboratory investigatory research to determine applicability is strongly recommended.

15.5 EVAPORATION

Evaporation is a procedure for removing water from nonvolatile dissolved materials. Evaporation is well known and widely practiced.[1] Evaporation of these waste waters has been studied by Bechtel Corporation[8] and seems to work. Skrylov and Stenzel[8] distilled wastewater *after* phenol extracting and *after* steam stripping to remove ammonia and carbon dioxide, and *after* addition of alkali to hold down volatile acids. They report that for the lab tests "the caustic required was substantial." The wastewater altered with age and the best distillate was obtained on fresh samples. That is, with age the organic contaminants break up into more volatile fractions. With a 95 percent recovery of water the distillate contained only 4 percent of the total organic carbon in the feed. (The feed contained 330 mg/l TOC and the distillate contained 14 mg/l TOC. This is approximately equivalent to reducing COD from 1100 to 47.) The remaining TOC stayed in the remaining 5 percent of the water which was not distilled over. If the first 5 percent of the water distilled was rejected so that a 5-95 percent cut was taken, the organic carbon in the recovered distillate was halved.

The TOC in the feed is lower than is assumed in some of the waters in this study and represents what is left after solvent extraction. The TOC in the distillate is still too high for boiler feed. It was found that it could be further reduced by oxidation with ozone. Ozonation was slow and 150 minutes were required to reduce TOC from 14 to 3. Skrylov and Stenzel concluded that a good arrangement might be to extract and then strip all of the wastewater of ammonia. Some of the water would then be evaporated and ozonated for boiler feed water, and the rest of the water would probably require biological oxidation to make it fit for makeup to the cooling tower.

In the range of interest of 0.5×10^6 to 3×10^6 gallons/day, costs are proportional to throughput and independent of concentration and so can be conveniently measured in $/thousand gallons. Capital cost is about $2/(gallons/day) and, taking amortization and maintenance at 17%/yr for 300 days/yr the charge is about $1.13/thousand gallons. The fuel cost will depend on the plant design. Considering as an example a multistage flash evaporator using waste steam recovered from the coal conversion, and if the price of waste steam is $1.80/10^6 Btu, then Reference 1 suggests that the optimum designs are:

Throughput (10^6 gal/day)	No. of flash stages	Btu/lb of water removed	Fuel cost ($/thousand gals)
0.5	22	136	2.00
1.0	25	120	1.80
3.0	37	81	1.20

The remaining charges, particularly including the cost of alkali, are not known. They are taken as $1.00/thousand gallons, bringing the total cost to between $4.10 to $3.40/thousand gallons depending on throughput.

Throughput	Total cost	Energy	
(10^6 gal/day)	($/thousand gals)	(10^6 Btu/thousand gals)	(10^9 Btu/day)
0.5	4.10	1.1	0.6
1.0	3.90	1.0	1.0
3.0	3.40	0.7	2.0

These numbers are shown on Figure 15-2.

Distillation is energy intensive but, for the foul waters that are being treated here, so are many other treatments. One of the ammonia separation possibilities uses about 37 lb steam per 100 lb feed water in the deacidification and ammonia towers. This is 370 Btu/lb water treated or 3.1×10^6 Btu/thousand gallons. The energy to supply oxygen in an air-activated sludge biological treatment plant is about 54 kw-hr/thousand gallons depending on the BOD. If it takes 10,000 Btu/hr to generate 1 kw of electricity, this means 0.5×10^6 Btu/thousand gallons, but this energy must be supplied at a high level, not as waste heat.

If it works, distillation should be considered when condensate is to be returned to the boilers. Prerequisites for distillation are ammonia removal and solvent extraction. Biological treatment is probably not only not required but may be harmful in that large, nonvolatile organic molecules tend

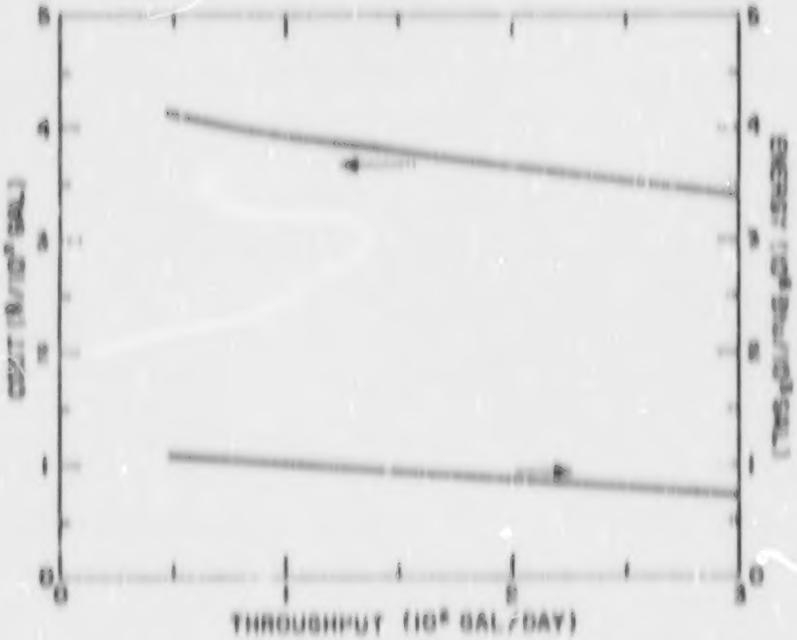


Figure 15-2. Cost and energy of evaporation.

to be broken by biological treatment to smaller, volatile molecules.

15.6 TREATMENT OF CIRCULATING COOLING WATER

In this section is a brief description of the usual treatment required for circulating cooling water with the references in which details are given. Treatment is intended to prevent scaling, fouling, microbial growth and corrosion and will be described under these headings.

Prevention of Scaling

The usual way to prevent scaling when high cycles of concentration are used is to remove calcium, magnesium, bicarbonate, phosphate and silica. Since calcium and magnesium are referred to as "hardness," their removal is called "softening." Bicarbonate is sometimes referred to as "alkalinity," although this term encompasses other alkalis. Scaling can be prevented even when precipitation occurs by the addition of chemicals which inhibit crystal growth and hold the microcrystals in suspension. These chemicals are discussed under the heading "Prevention of Fouling."

The simplest procedure is to add sulfuric acid (H_2SO_4). This acid is much stronger than carbonic acid and carbon dioxide is released from the water according to the equation

$$H_2SO_4 + 2HCO_3^- \rightarrow 2H_2O + SO_4^= + 2CO_2 \uparrow$$

One pound of HCO_3^- requires 0.8 lb H_2SO_4 for treatment. The cost of sulfuric acid and other chemical costs are given in Table 15-3.

TABLE 15-3. CHEMICAL COSTS

Delivered costs used in this study

	¢/lb
Sulfuric acid	1.8
Lime	2.7
Soda ash	4.0
Dolomite	7.0
Alum	5.3

A common softening procedure is precipitation with lime ($Ca(OH)_2$) and soda ash (Na_2CO_3). The quantities of lime and soda ash required are estimated from the following equations.[9,12]

Calcium and dissolved carbon dioxide and bicarbonate are first precipitated together:

$$Ca(OH)_2 + CO_2 \rightarrow CaCO_3\downarrow + H_2O$$

$$Ca(HCO_3)_2 + Ca(OH)_2 \rightarrow 2CaCO_3\downarrow + 2H_2O$$

The solubility of calcium carbonate is dependent on pH. Lime is usually added to raise the pH to about 9.4[12] and calcium is reduced to about 12 mg/l (as Ca). The concentration of calcium and magnesium left after lime-soda treatment is less the higher the temperature, and sidestream treatment should be done preferably on the hot water.

If removal of calcium in excess of bicarbonate is required, soda ash must be added:

$$Ca^{++} + Na_2CO_3 \rightarrow 2Na^+ + CaCO_3\downarrow$$

If bicarbonate is present in excess of calcium, the magnesium will precipitate:

$$Mg(HCO_3)_2 + 2Ca(OH)_2 \rightarrow Mg(OH)_2\downarrow + 2CaCO_3\downarrow + 2H_2O$$

More magnesium can be precipitated by adding more lime:

$$Mg^{++} + Ca(OH)_2 \rightarrow Mg(OH)_2\downarrow + Ca^{++}$$

Since the solubility product $(Mg^{++}) \times (OH^-)^2$ tends to be constant, the residual magnesium in solution can be lowered by raising the concentration of hydroxyl ions, that is, by raising the pH. This is shown on Table 15-4. In practice a pH of 10.5 or higher is used and magnesium is reduced to about 2.5 mg/l (as Mg). This procedure adds calcium to the water, unless soda ash

TABLE 15-4. SOLUBILITY OF MAGNESIUM AT DIFFERENT pH (TAKEN FROM REF. 13)

	pH = 9	pH = 10	pH = 11	pH = 12
Mg^{++} (mg/l)	216	2.16	0.0216	0.00216

---

is used.

Silica coprecipitates with magnesium hydroxide at a rate of about 1 gm SiO_2 per 7 gm Mg^{++}. (This figure was supplied by A.B. Mindler, Permutit Research and Development Center, Princeton, New Jersey, and is also given by Kluesner *et al.*[14] If more silica removal is required then magnesium will have to be added. The ability to remove silica with magnesium at a cooling water temperature of 80°F (25°C) or above is illustrated in Reference 11, page 84.

When the pH is raised to about 11, phosphate removal is quite complete[14] and the equation is

$$5Ca(OH)_2 + 3HPO_4^{=} \rightarrow Ca_5(OH)(PO_4)_3 + 6OH^- + 3H_2O$$

indicating a consumption of 5 moles of lime for 3 moles of P. An alternative view is that the precipitate is calcium orthophosphate $Ca_3(PO_4)_2$ and not hydroxyapatite $Ca_5(OH)(PO_4)_3$ which indicates a requirement of 4.5 moles of lime for 3 moles of P.[15] In fact, these differences in lime requirement would not be readily distinguishable.

Calculation of lime requirements must include the lime needed to raise the pH.

After treatment the water is neutralized with sulfuric acid. Carbon dioxide is sometimes used, but this decreases the net removal of carbon dioxide and in sidestream treatment increases the size of the sidestream.[16]

Lime-soda softening involves a small investment in chemical feeders and mixers and a large investment in clarifiers to settle out the precipitates. Cost-estimating curves have been kindly supplied by the following companies: Dorr-Oliver, Inc.; Envirotech; F.M.C. Corporation; Graver Water Division of

Ecodyne Corp.; and Permutit Co., Inc. Installed clarifier costs have been estimated using the cheaper of steel or concrete tanks. The concrete cost was taken to be $175/cubic yard and includes excavation, backfill, concrete, concrete forms, rebar and finish. Steel tank costs were in part supplied by Bethlehem Steel. The cost curve used in this study is given on Figure 15-3.

To aid sedimentation in the clarifiers, synthetic flocculants were assumed to be added at a rate of 1 mg/l. Flocculant costs were supplied by Dow Chemical, Rohm and Haas, and the Tretolite Division of Petrolite Corporation. A cost of 1.3¢/thousand gallons of sidestream has been used.

Prevention of Fouling

All cooling towers scrub dust out of the air. In this study we have used a standard rate of input of dust to the water using a dust concentration in the air of 10^{-6} lb/ft^3 (Reference 17) and the tower conditions given in Section 10. The calculation is

$$\frac{1400\ \text{Btu}}{\text{lb water evaporated}} \times \frac{1\ \text{lb water circulated/hr}}{25\ \text{Btu/hr}}$$

$$\times \frac{1\ \text{lb air passed}}{2.8\ \text{lb water circulated}} \times \frac{380\ \text{ft}^3}{29\ \text{lb air}} \times \frac{10^{-6}\ \text{lb dust}}{\text{ft}^3\ \text{air}}$$

$$= 2.6 \times 10^{-4}\ \text{lb dust transferred/lb water evaporated}$$

About 1/5 of the dust transferred is suspended in the circulating water;[17] the rest settles in the basin or is not trapped. The suspended dust input rate is 0.052 lb/thousand pounds of water evaporated. Because of the dust scrubbed from the air, the concentration of 300 mg/l suspended solids in the circulating water dictates a maximum of 6.8 cycles of concentration even with crystal clear makeup water, unless sidestream clarification is used.

In many cases some form of clarification has proved necessary. When clarifying the effluent from biotreatment, a filter has been assumed. Effluent from biotreatment has about 100 mg/l suspended solids. The installed costs of automatic backflushed, gravity sand filters have been supplied

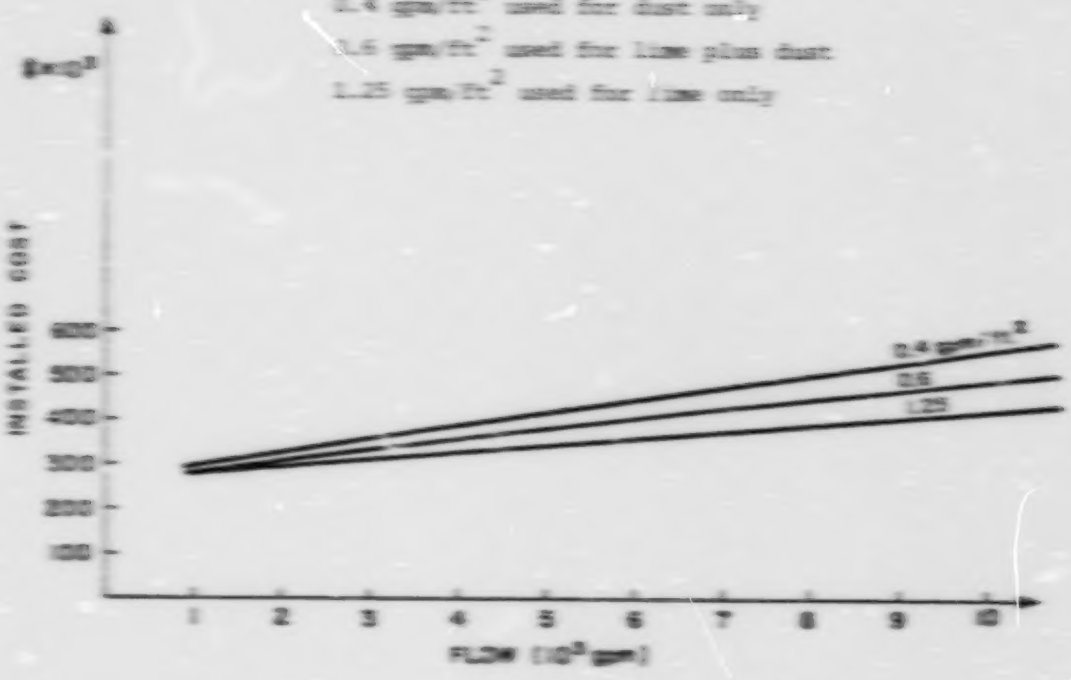


Figure 15-1. Clarifier costs.

by Graver Water Division of Ecodyne, Environmental Elements Corporation Division of Koppers Company, and Permutit Co., Inc. The supplied costs from these sources, which included tanks, mechanisms, installation and sand, were all very close to each other. We have used \$150/ft^2 at 2 gpm/ft^2 for a cost of \$75/gpm. Excess capacity is not used because the filters are all multiple units, and automatic continuous backwash is included in the cost.

In clarifying a cooling tower sidestream where the suspended solids are 300 mg/l, a filter has been used on low flow streams, but the flow rate is reduced to 1 gpm/ft^2 increasing the cost to \$150/gpm. Above about 2,000 gpm, clarifiers (shown on Figure 15-3) are cheaper and are used. The overflow from a clarifier is assumed reduced to 100 mg/l S.S.

Synthetic polymeric dispersant chemicals (also called antifoulants) are added to the circulating water. Information on dosage and cost of dispersants has been supplied by Drew Chemical Corp. and Hercules, Inc. A cost of 3¢/1,000 gals sidestream + blowdown has been used. The cost basis is the sidestream because the flocculants added to the clarifiers will destroy the dispersants.

Control of Microbial Growth

Microbial growth must be prevented by the addition of microbicides to the circulating water. The constant presence of air, nutrients and additional growth introduced from the air renders makeup and sidestream treatments ineffective. Unrestricted growth of microorganisms can lead to fouling of heat transfer surfaces and plugging of pipes; it can also lead to corrosion of wood in the cooling towers and corrosion of metal surfaces, particularly by bacteria that metabolise sulfur. Descriptions of the microorganisms that are found in cooling water are given in References 18 to 21. Sussman[22] has recommended prompt disinfection if the total plate count is higher than about 10^6/ml and states that most systems can operate adequately with plate counts less than 500,000/ml. A very large number of biocidal chemicals are available. They are usually used in combinations to prevent acclimatisation of the microorganisms and often used in the form of a "shock treatment" in which a high dose is added for a short while and then the concentration is allowed to die down. This produces high effectiveness at the lowest cost.

Chlorine is probably the most common microbicide used today. It has disadvantages. It is most active at acid pH, which is not planned because of corrosion. Shock treatment will overcome this problem to some extent. It reacts with ammonia when sewage water is used as makeup, which lowers its activity. It also reacts with oxidizable organic molecules which will be present. Chlorine is toxic. Less toxic nonoxidizing chemicals have been chosen because organic molecules are usually present and because blowdown is usually dumped with ash.

A very large number of nonoxidizing microbicides have been used[18,19,21] and only a few of the most popular will be described here. Quaternary ammonium salts are cationic surface active agents with a wide range of microbicidal activity. They are the least toxic to animal life. Several quaternary ammonium compounds are approved for use in dairies. The most commonly used in dairies are alkyldimethylbenzyl ammonium chloride, alkylpyridinum bromide and cetylpyridinum chloride.[23] Schultz[24] has described two quaternary ammonium salts and a diamine which have been found to be nonpersistent and to behave well in cooling towers. He has tested a trialkylbenzyl ammonium chloride (this group includes the first of the dairy sanitizers mentioned above), a tetra-alkyl ammonium chloride and an aliphatic diamine. Because quaternary ammonium compounds are surface active, they are removed from effectiveness in solution by oily or turbid waters. Quaternary ammonium compounds when used with organotin compounds have a synergistic effect and a wide range of microbicidal activity.

Methylenbisthiocyanate has broad range microbicidal activity at low concentrations. It is not affected by dirt, hardness and oil. It loses all activity after one hour at pH 8, which makes blowdown disposal convenient but makes it useless for some alkaline waters.

Costs of biocides having EPA, USDA and similar approvals as nondangerous materials have been supplied by Buckman Laboratories, Drew Chemical Corp., Hamlen Chemical, Hercules, Inc. and Lonza, Inc. Costs lie in the broad range of 15¢ to $1.50 per thousand gallons of blowdown. The major mechanism of loss of biocide is in blowdown. An average cost of 50¢/1,000 gallons of blowdown has been used in this study for water without a lot of organic carbon, phosphate or ammonia. When these nutrients are present the cost of biocide has been increased (see Section 19 for the individual cases).

Corrosion Control

Corrosion in cooling systems is discussed in many references.[18,25,26] In this study carbon steel is assumed to be used in the heat exchangers so corrosion control will be necessary. However, in most of the plants the cooling tower blowdown is assumed to be used for dust control and ash disposal, so chromium, or indeed any heavy metal, should be available for corrosion control. Experience on controlling corrosion without chromium is varied. In 1975 Brunn[27] made the following statement:

> "Our goal is to find a replacement for chromate/zinc which can be purchased from a supplier. Five years have been spent on this program, and it is continuing. None of the materials tested during the first two years even approached the desired qualities. During the past two years there have been some promising candidates which are applicable to some company systems, but none which are universally acceptable. In general, these fall into the category of organic phosphate plus some inorganic salt such as zinc or inorganic phosphates. In most of these materials corrosion inhibition is found to be relatively good, but there is a significant increase in deposition on heat transfer surfaces. This is caused by more demanding microbiological control, precipitation reactions between treatment and circulating water, and fouling which results from laydown of the additional corrosion products because of the slight loss in corrosion protection. Our initial movement to nonchromate inhibitors is slow, but in the past two years we have made significant moves toward nonchromate inhibitors."

It must be understood that the procedures tentatively adopted for this study are not fully proven. This is the more so because zinc, as well as chromium, is avoided because of the presence of ammonia.

In using nonmetallic corrosion inhibitors, certain practices seem to be necessary and are followed in this study. The circulating cooling water is best kept just alkaline and a lot of effort is made to control scaling and fouling. Furthermore, throughout the plants the temperature on the opposite side of the heat transfer surface from the cooling water is below about 100°F.

Petry[28] has reported on the importance of temperature. Finally, it will be necessary to passivate the new system at start-up when it is still clean.

Many tests have been reported including those by von Knappen and others,[26] Hwa,[29] and Gesick.[30] Harpel and Donahue[31] found adequate corrosion resistance using orthophosphate in the range 1-5 mg/l, total phosphate 4-10 mg/l and phosphonates. The conditions necessary for success were (i) prior passivation with chromate, (ii) pH 7 to 9, and (iii) cal[illegible] than 50 ppm as $CaCO_3$ (Langelier index 1 to 2.5). The phosphonates prevented scale formation by calcium carbonate and calcium phosphate. Furthermore, the phosphate concentration was not so high as to increase the growth of algae.

Based on cost information kindly supplied by Drew Chemical Corp., Gamlen Chemical and Hercules, Inc., the cost of nonchromium corrosion inhibition chemicals lies in the range of 35¢ to 65¢/thousand gallons of blowdown. This is to be compared to 3¢ to 9¢/thousand gallons of blowdown for chromium based chemicals. A cost of 50¢/thousand gallons of blowdown is used.

15.7 REVERSE OSMOSIS

Reverse osmosis is a pressure-driven membrane process for separating relatively pure water from solutions containing salts, dissolved organic molecules and colloids under the action of a hydrostatic pressure applied across a membrane separating the feed from the relatively pure water. The process is frequently termed "hyperfiltration." Water passes through the membrane and the dissolved materials remain behind.[1] The rejection of the dissolved materials is not complete, the incompleteness depending not only on the size of the rejected species but also on the chemistry of the membrane and the rejected species. Of particular interest to designers of water systems for coal conversion plants is the degree of removal of organic matter.

Although many authors report on the tertiary treatment of sewage by reverse osmosis, all the publications known to us limit the documentation to measurements of salt concentration. Measurements of carbon, COD or BOD are not given. Duvel and Helfgott[33] have measured the rejection of a large number of specific organic compounds. The rejection is semi-quantitatively related to both molecular weight and molecular size, as determined by steric geometry. Size is the more important; branched chain molecules are better rejected than straight chain molecules. Lindemann[34] has found that reverse osmosis of sewage plant effluent renders the water suitable as feed to the boiler makeup demineralizers which says that carbon removal is adequate.

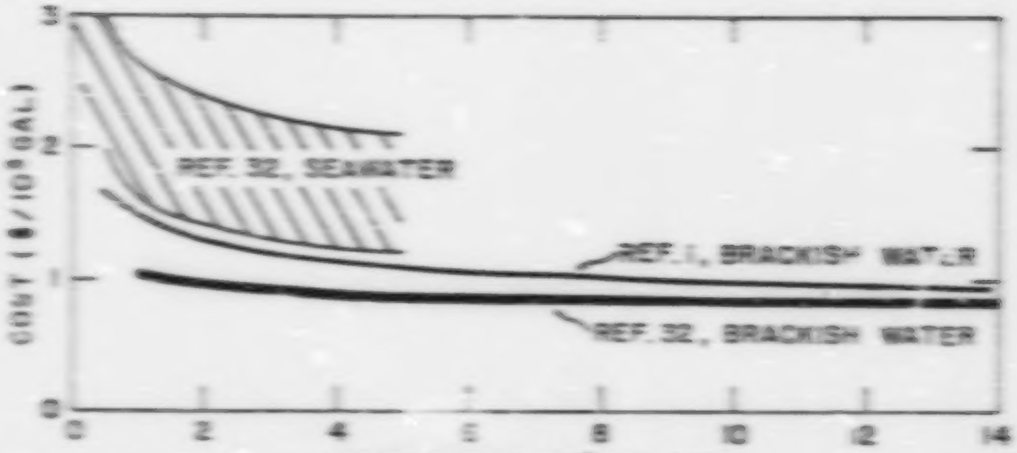
Reverse osmosis membranes will also partly reject silica which is important in the treatment of both cooling water and boiler feed water.

A cost estimate is given on Figure 15-4. This shows cost as a function of throughput and independent of concentration. It is meant to apply when concentrating to about 2 percent total dissolved solids and the throughput is a measure of the recovered water, not the feed water. A similar cost curve (not exactly the same conditions) has been published for 80 percent recovery from brackish water (2,000-5,000 mg/l TDS feed, 1-3.5 percent TDS maximum concentration)[32] and this also is given on Figure 15-4 along with the cost estimates from Reference 32 for sea water desalting in a two-stage plant. In this study the cost curve from Reference 1 has been used unless the concentration is pushed above 2 percent. For higher concentrations higher costs have been used which are given for each individual case. The energy requirement, which is mostly to pump the feed to about 800 psi, is about 7.2 kw-hr/thousand gallons.

15.5 ELECTRODIALYSIS

Electrodialysis is a membrane separation process in which dissolved ionic impurities are removed from water through membranes under the driving force of a dc electric field.[1] Only dissolved, charged particles are removed and concentrated. Unlike reverse osmosis, electrodialysis has no effect on uncharged, dissolved molecules and little effect on suspended matter. In this study electrodialysis has been used for desalting brackish source water for the plants sited in New Mexico.

Because the energy required depends on the quantity of salt removed, while the capital depends on the throughput, the cost of electrodialysis is dependent on both the flow rate and the change in concentration. The cost therefore has not been presented in graphical form but has been calculated



(From Reference 1, pages 93-94, two-year membrane life with membranes costing 15% of the total capital, 8,000 hr/yr.)

Figure 15-4. Costs of reverse osmosis.

for each individual use. The total operating cost is the sum of these figures: (1) the capital cost read from Figure 15-5 and charged at 17%/yr for amortization, maintenance and other capital-related items; (2) membrane replacement, prefiltration and chemical additives at $0.20/thousand gallons of throughput; and (3) electricity at 2¢/kw-hr for
0.4 kw-hr/(thousand gallons)(100 mg/l removed).

15.9 ION EXCHANGE

Ion exchange is used in this study to remove ionic species and silica from boiler feed water by exchanging these species with hydrogen, sodium and hydroxyl ions on solid resins. The resins are then regenerated by H_2SO_4, NaCl and NaOH enabling their continued use and reuse over long periods of time. Design of an ion exchange system is straightforward and is explained elsewhere.[9,10,35] The boiler feed water treatment areas on the plant designs of Section 19 have been designed and costed individually, there being no simple rules such as were used with other water treatment technologies. A very brief description, limited to resins found useful for this study, follows.

A "weak-acid" resin is used to exchange positive ions in the water with H^+. The resin removes only that part of the total cations equivalent in amount to the bicarbonate alkalinity. This resin is particularly good for removal of Ca and Mg ions and less satisfactory for removing Na ions. When H^+ has been substituted for Ca^{++} and Mg^{++}, carbonic acid is formed which decomposes to free carbon dioxide that is then released in a degasifier. A great advantage of weak acid resins is the ease of regeneration with sulfuric acid; 110 percent of stoichiometry is all that is required.

A "strong-acid" resin is used to replace all of the cations with H^+. Regeneration of strong acid resins with H_2SO_4 is very inefficient, requiring about 200 percent of stoichiometry with counter-current regeneration. But in all the designs the regenerant acid is poured first through the strong-acid resin and then through the weak-acid resin, thus ensuring a high use of the acid.

A "softening" resin is used to replace Ca^{++} and Mg^{++} with Na^+. It is regenerated with NaCl and requires about 200 percent of stoichiometry to

1 = One Stage, approximately 50% demineralization

2 = Two Stages, approximately 75% demineralization

3 = Three Stages, approximately 87.5% demineralization

4 = Four Stages, approximately 93.8% demineralization

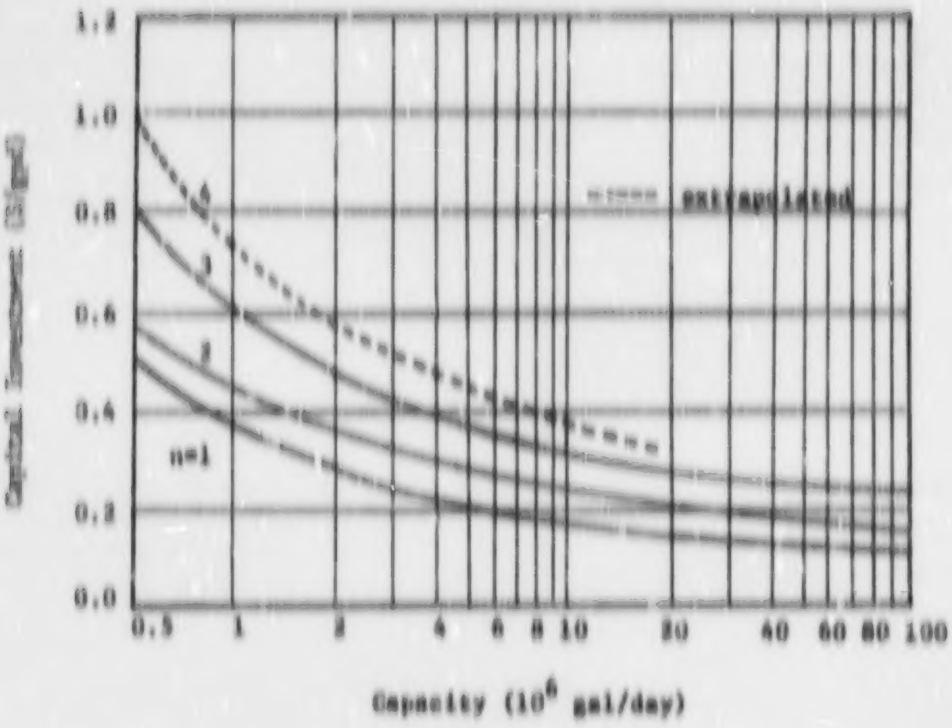


Figure 15-5. Approximate electrodialysis capital investment as a function of capacity for various numbers of stages. (Each stage removes approximately 50% of salts in its feed water.)

regenerate in a counter-current manner.

A "weak-base" resin is used to replace $SO_4^=$ with OH^-. It cannot remove weakly dissociated carbonic acid from the alkalinity or silicic acid from the silica content in the water. It is easily regenerated with NaOH requiring about 110 percent of stoichiometry. This resin follows a strong acid resin to produce a demineralized water. A "strong-base" resin is used to replace both the weakly dissociated and strongly dissociated acids. In these designs a strong base resin has been used to replace SiO_2 with OH^-. It is regenerated with NaOH. The regeneration is inefficient, but the caustic soda is passed from the "strong-base" to the "weak-base" resin to obtain a high use of the chemical.

A "mixed-bed" is a mixture of strong acid and base resins designed to polish demineralized water without large swings in pH. The treatment is necessary for high pressure boilers.

Regenerating chemicals are taken to cost

H_2SO_4	3.8¢/lb
NaOH	8.3¢/lb
NaCl	2.0¢/lb

Capital costs for the ion exchange systems discussed in Section 10 have been supplied to us by Permutit Co., Inc., Paramus, New Jersey. These systems are skid-mounted and fully instrumented.

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SECTION 16

SEPARATION OF AMMONIA, CARBON DIOXIDE AND HYDROGEN SULFIDE

16.1 INTRODUCTION AND RESULTS

Process condensate is laden with ammonia. In the gas plants the ammonia is mostly neutralized by carbon dioxide. In the solvent refined coal plant the ammonia is partly neutralized by hydrogen sulfide. Depending on the coal, hydrogen chloride may have been present in the gas phase and this will pass into the condensate and neutralize ammonia. Any organic acids in the vapor will also mostly pass into the condensate and neutralize ammonia. Phenol is itself a weak acid. Ammonia must be removed from condensate. Ammonia is volatile, but simply venting it to the atmosphere is not acceptable. Fifty percent of the population will respond to the odor of 21.4 ppm by volume NH_3 in air.[1] The state of New Mexico permits 25 ppm by volume in an effluent gas stream. This strength vapor is blown from a solution containing about 13 mg/l ammonia. Of course the vapor if dispersed, but it is quite clear that simply blowing ammonia into the atmosphere is not permissible from strong solutions. Ammonia must be collected, and since ammonia is a salable commodity, it should be collected in a salable form. Also, H_2S cannot be vented to the atmosphere but must be collected and sent to the sulfur recovery plant. Ammonia interferes with the Claus sulfur recovery process.

The problem is not the removal of ammonia and gaseous acids from water, which is the usual problem of stripping or "sour water stripping." For these wastewaters ammonia and gaseous acids must be separated into three individual streams.

The presence of phenol and volatile organic acids may interfere with ammonia separation because the procedures considered in this section all rely on relative volatility to effect part of the separation. In the following discussion the possible problems caused by phenol and volatile organic acids are not considered. If phenol is extracted, this is done before the separation of ammonia. Extraction will remove most of the volatile organic carbon from the water. That part of the ammonia neutralized by hydrochloric acid will remain in the water unless alkali is used. If the water goes on to biotreatment, 450 mg/l N is required for nutrient. This represents the quantity of ammonia fixed by 1140 mg/l Cl, so fixed ammonia may not be a problem unless chloride exceeds this value.

It is not difficult to separate volatile gases (NH_3 and volatile acid gases) by stripping the water in a tray column with steam (live or from a reboiler) at a rate usually in the range 8-12 lb steam/100 lb water. Stripping is much described in the literature.[2-4] If this is done then ammonia must be separated from the CO_2 + H_2S. One way to do this, not considered in this study, is to absorb the ammonia in sulfuric acid and produce crystalline ammonium sulfate for sale. Another procedure is to absorb the ammonia in phosphoric acid or acid ammonium phosphate. It is then possible to strip out the ammonia with steam and to recycle the acid ammonium phosphate. This is the Phosam-W process of United States Steel Corporation Engineers and Consultants described in Section 16.7. For this study, this is the preferred process. The Phosam-W process is shown in Figure 16-1.

It is possible to separate wastewater into three streams by an all-distillation procedure as pictured in Figure 16-2. By refluxing clean water to the "deacidification" column, CO_2 and H_2S are removed overhead while ammonia remains in solution. In the second ("ammonia") column, ammonia is stripped out of water and concentrated. A procedure similar to the all-distillation procedure is shown in the drawings of most Lurgi plant water treatment schemes as part of the Phenosolvan processes. The procedure investigated in this study is *not* the Phenosolvan process.

In order to compare the all-distillation process with the Phosam-W process, a study has been made of the all-distillation procedure. Section 16.2 describes the basic equations that were used for tray-to-tray calculations

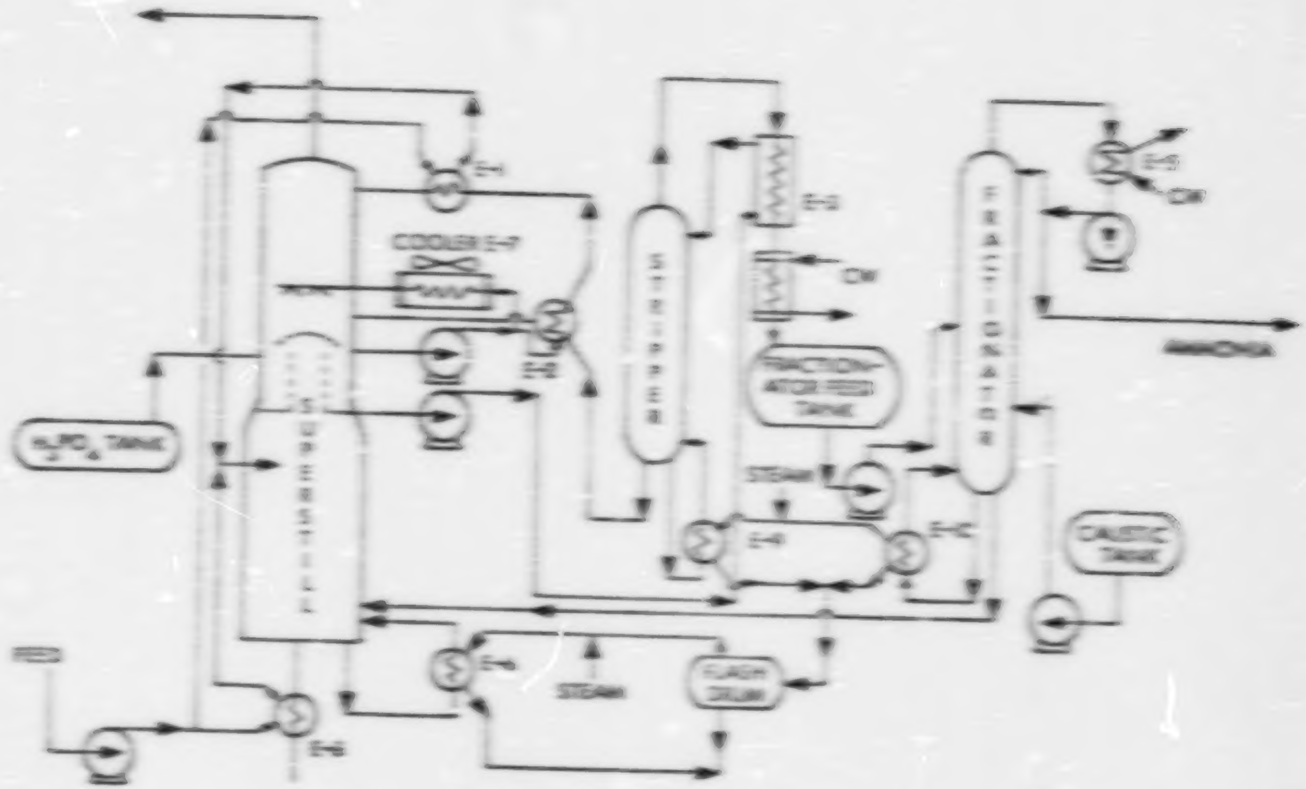
FEED
E-6
H_3PO_4 TANK
SUPERSTILL
COOLER E-7
E-1
E-8
STRIPPER
STEAM
FLASH DRUM
E-4
FRACTIONATOR FEED TANK
CW
FRACTIONATOR
E-5
CW
AMMONIA
CAUSTIC TANK

Figure 16-1. Phosam-W process for ammonia separation.

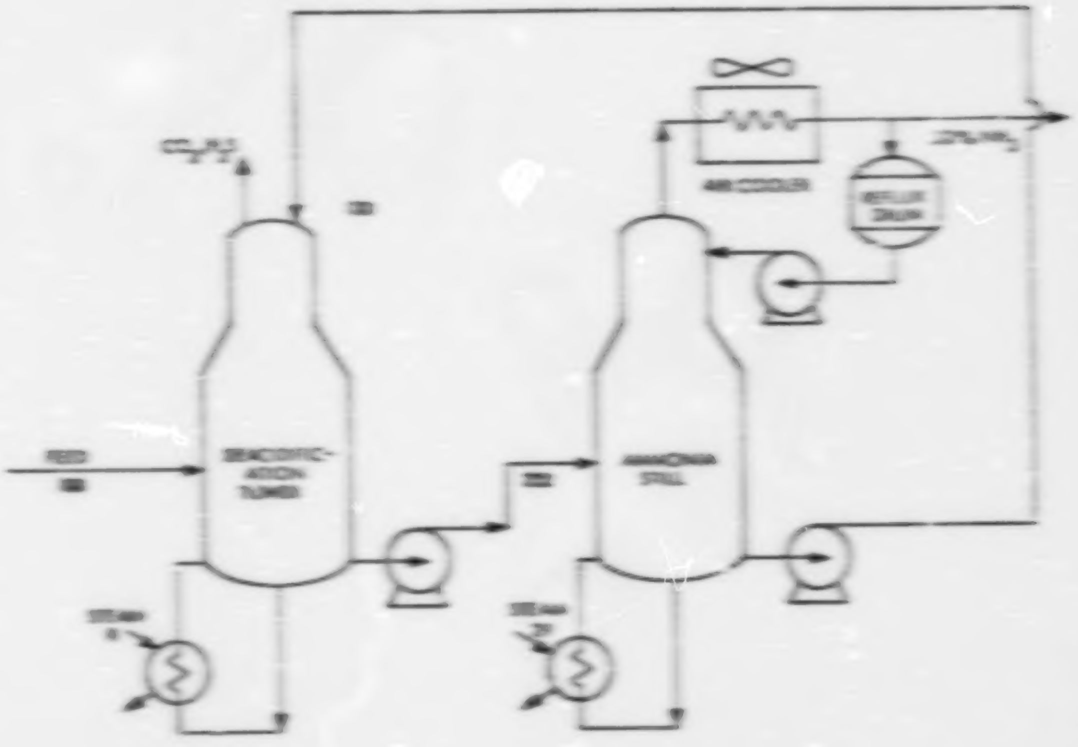
CO_2, H_2S
FEED
DEACIDIFICATION TOWER
AMMONIA STILL
AIR COOLER
REFLUX DRUM
STEAM
STEAM
NH_3

Figure 15-2. All-distillation process for ammonia separation.

down the tower to determine the necessary number of theoretical trays which control the height of the tower. The vapor liquid equilibrium data for a mixture of NH_3, CO_2 and H_2O is presented in Section 16.7 and applies to gas-producing plants. Similar data for a mixture of NH_3, H_2S and H_2O, presented in Section 16.4, are held to apply to an SNG plant. Calculated results applicable to gas plants are presented in Section 16.5. For the Phosam-W process the design was provided by United States Steel Engineers and Consultants. We have estimated the capital cost of both systems.

On Figure 16-3 are shown the capital costs for the all-distillation process to separate water, NH_3 and CO_2, together with two costs for the Phosam-W process. The Phosam-W process is cheaper than the all-distillation process, as assumed in this study, and uses less energy. Furthermore, the all-distillation process may not work for mixtures of water, NH_3 and H_2S without the presence of CO_2. For ammonia separation in all plants, we have therefore assumed the use of the Phosam-W process with capital and operating costs as shown in Figure 16-4. We have limited points on the capital cost versus throughput curves for the Phosam-W process and have drawn the curves through these points proportional to the curve for the all-distillation process.

16.2 SEPARATION BY DISTILLATION; CALCULATION OF NUMBER OF THEORETICAL TRAYS

The distillation equations for the deacidification column in the all-distillation procedure are briefly given here in the form in which they were used.

The nomenclature is shown on Figure 16-5. All flows are in moles/hr. The mixture is assumed to be H_2O, NH_3 and CO_2. The washwater (reflux) and feed are saturated liquids. The usual simplifying assumption of constant molal overflow is made. The calculation is made in the manner given in standard texts on distillation. The desired condition at the top of the tower--D, DN, DC--is stated. The reflux or wash water--O--is stated. The feed--F, FN, FC--is given. The tower bottoms--W, WN, WC--are calculated from the overall tower material balance. The reboil rate S is stated. The number of theoretical trays is then calculated. If this number was greater than about 20, calculation was stopped and a new choice of O and S was made.

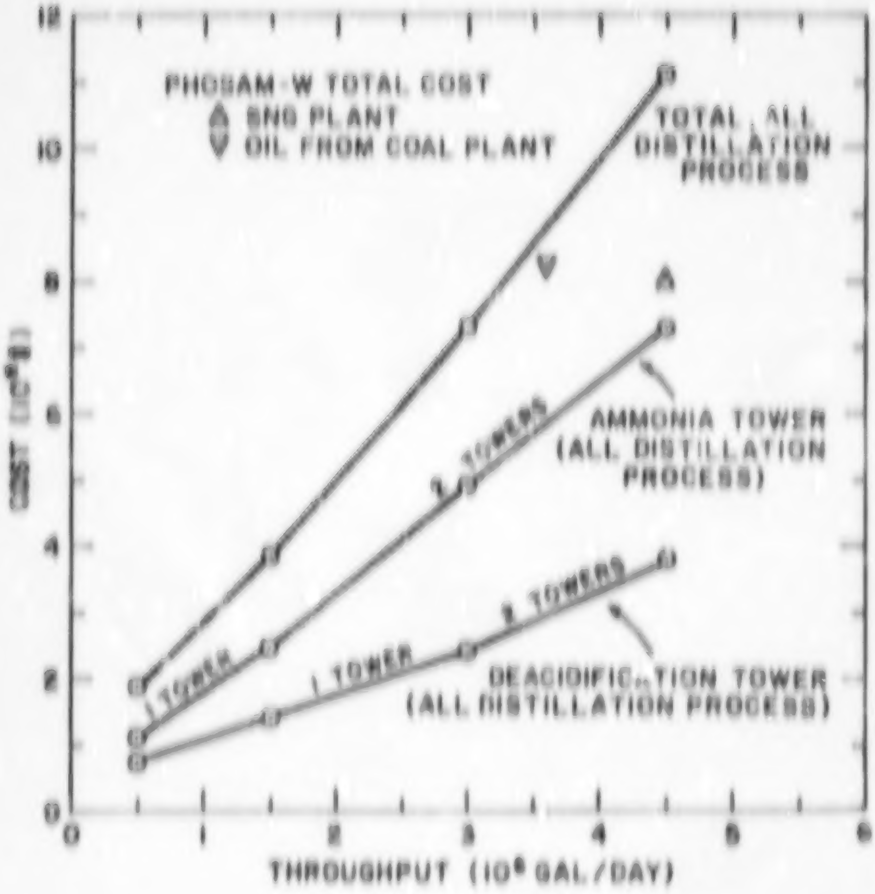

Figure 16-1. Comparative capital costs for ammonia separation.

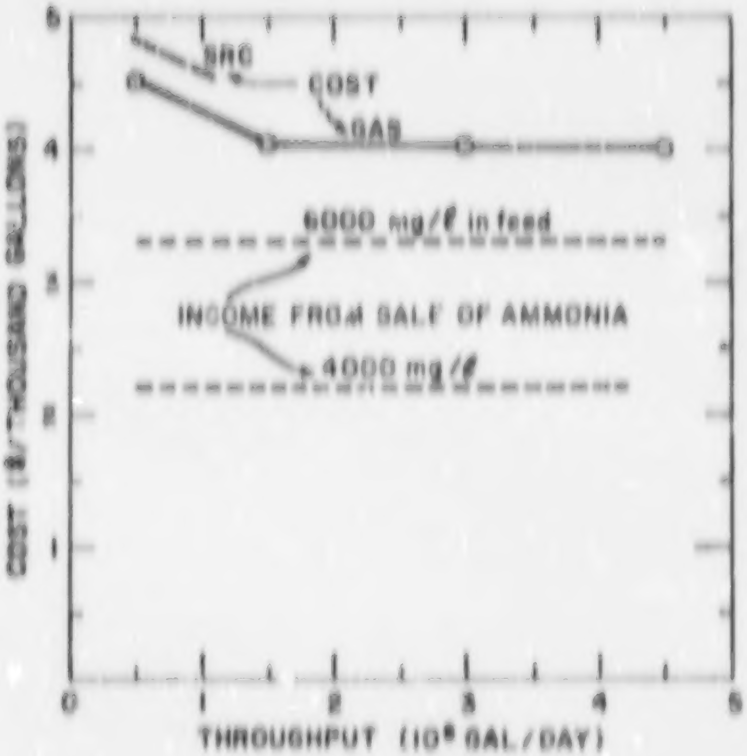

Figure 16-4. Operating costs for ammonia separation.

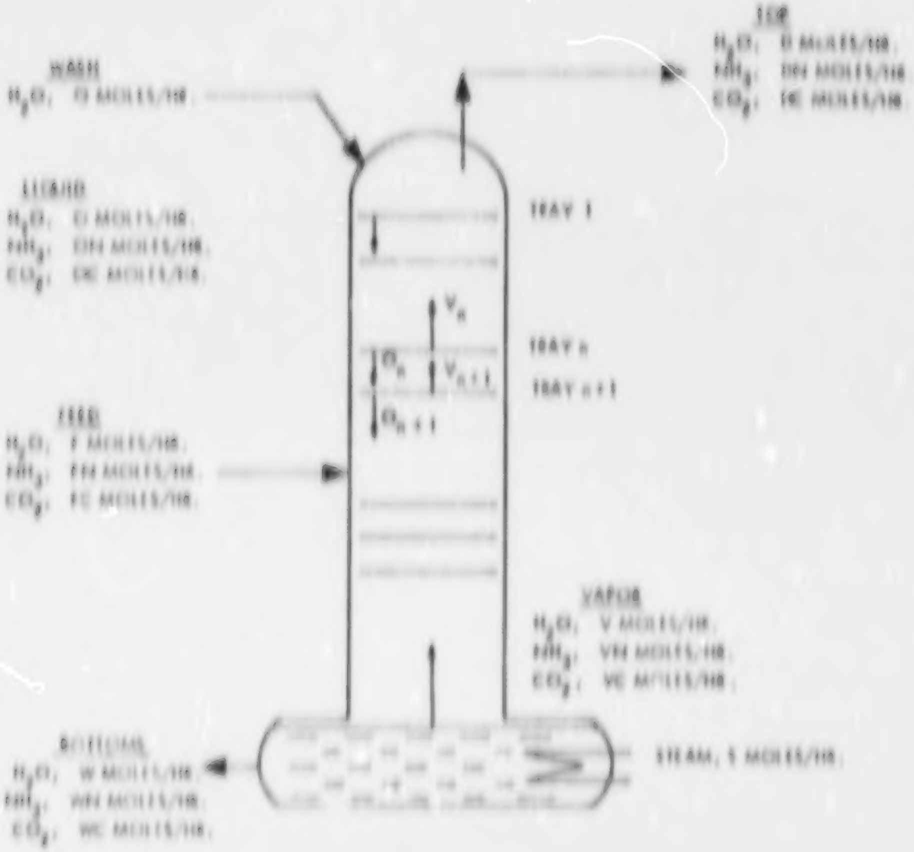
WASH
H_2O; O MOLES/HR.
TOP
H_2O; D MOLES/HR.
NH_3; DN MOLES/HR.
CO_2; DC MOLES/HR.
LIQUID
H_2O; O MOLES/HR.
NH_3; ON MOLES/HR.
CO_2; OC MOLES/HR.
TRAY 1
V_n
TRAY n
O_n
V_{n+1}
TRAY n+1
O_{n+1}
FEED
H_2O; F MOLES/HR.
NH_3; FN MOLES/HR.
CO_2; FC MOLES/HR.
VAPOR
H_2O; V MOLES/HR.
NH_3; VN MOLES/HR.
CO_2; VC MOLES/HR.
BOTTOMS
H_2O; W MOLES/HR.
NH_3; WN MOLES/HR.
CO_2; WC MOLES/HR.
STEAM, S MOLES/HR.

Figure 16-5. Distillation tower nomenclature.

The calculation starts at the top of the tower. A material balance around the top of the tower, below tray n and above tray n+1, when n is above the feed, gives

$$V_n = D = 8 \qquad (1a)$$

$$VH_{n+1} = OH_n + DH \qquad (1b)$$

$$VC_{n+1} = OC_n + DC \qquad (1c)$$

Since only pure water is refluxed

$$OH_0 = OC_0 = 0$$

and

$$VH_1 = DH$$

$$VC_1 = DC$$

The molar vapor rates leaving the top tray are now known. The molar vapor rates are next converted to partial pressures. From the partial pressures the liquid concentrations can be found from the vapor-liquid equilibrium relations given in Section 16.3. From the liquid concentrations the liquid molar rates OH_1 and OC_1 can be calculated. Knowing OH_1 and OC_1, the vapor rates rising from the second tray VH_2 and VC_2 can be found from Equations 1. Calculation then proceeds from tray to tray down the tower.

The total pressure P_T on the top tray is taken to be 20 psia and the pressure is assumed to increase by 0.25 psia per tray going down the column. The total pressure on tray n is

$$P_T = 20 + 0.25(n-1) \qquad (2)$$

Within the narrow range of interest the vapor pressure of water, P_{H_2O}, is given by

$$T°K = 352 + 1.5P_{H_2O} \text{ (psia)} \tag{3}$$

$$\text{for } 18 < P_{H_2O} < 22$$

$$T°K = 0.555(t°F + 459.7) \tag{4}$$

But,

$$P_{H_2O} = P_T V/(V+VN+VC) \tag{5}$$

and so, from the vapor composition the temperature on any tray can be determined. Also,

$$P_{NH_3} = P_T(VN)/(V+VN+VC) \tag{6}$$

and

$$P_{CO_2} = P_T(VC)/(V+VN+VC) \tag{7}$$

Now, knowing the temperature and the partial pressures of NH_3 and CO_2, the total concentration of carbon dioxide, C moles/l, and the total concentration of ammonia, A moles/l, can be calculated as described in Section 16.3.

Finally, the liquid molar rates are related to the liquid compositions by the equations

$$GN_n = (0.018A_n)G \tag{8}$$

$$GC_n = (0.018C_n)G \tag{9}$$

Below the feed tray Equations (1) do not apply and Equations (10) should be used as follows.

$$V_n = D + B \tag{10a}$$

$$VH_{n+1} = OH_n - FH + DH = OH_n - WH \tag{10b}$$

$$VC_{n+1} = OC_n - FC + DC = OC_n - WC \tag{10c}$$

Feed is added to that tray which improves the separation of NH_3 and CO_2. When the calculation approaches the feed tray, double calculations must be made, one using equations (1) and one using equations (10). For each tray the ratio OC_n/OH_n (moles CO_2/moles NH_3 in liquid) is calculated, and when this ratio is lower using equations below than it is using equations above the feed, the feed should have been put in on the tray one above. Below the feed a double set of calculations is not necessary. This method of locating the feed tray seemed to give satisfactory results. It was not checked by calculating upwards from the bottom. This procedure throws the cumulative error into the bottom composition.

16.3 VAPOR-LIQUID EQUILIBRIUM FOR NH_3-CO_2-H_2O

The results of Van Krevelen, Hoftijzer and Huntjens[5] are used to find the concentrations of total ammonia and total carbon dioxide (A moles NH_3/l and C moles CO_2/l) given the partial pressures P_{NH_3} and P_{CO_2} (psia).

When carbon dioxide and ammonia are simultaneously dissolved in water the solution contains six species: NH_3, NH_4^+, NH_2COO^-, HCO_3^-, $CO_3^=$ and CO_2. "Total concentration" of ammonia means:

$$A = (NH_3) + (NH_4^+) + (NH_2COO^-) \tag{11}$$

"Total concentration " of carbon dioxide means:

$$C = (CO_2) + (HCO_3^-) + (CO_3^=) + (NH_2COO^-)$$

$$= \text{(approx.)} (HCO_3^-) + (CO_3^=) + (NH_2COO^-) \tag{12}$$

because (CO_2) is very small.

The equations which give the concentrations of the individual species are:

1) The modified Henry's law equation for NH_3,

$$P_{NH_3}\ (\text{psia}) = 0.0193\ \frac{(NH_3)}{H_0}\ 10^{0.025(NH_3)} \tag{13}$$

where

$$H_0 = \exp\left(\frac{4150}{T} - 16.54\right) \tag{14}$$

(Van Krevelen *et al*[5] give H_0, and the various equilibrium constants are given graphically. Here these constants have been expressed analytically for computer calculation.)

2) Because of the equilibrium

$$NH_3 + CO_2 + H_2O \rightleftharpoons NH_4^+ + HCO_3^-$$

$$P_{CO_2}\ (\text{psia}) = 0.0193\ \frac{(NH_4^+)(HCO_3^-)}{K_1(NH_3)} \tag{15}$$

where

$$K_1 = \exp\left(\frac{7540}{T} - 28.7 + \frac{12.4C}{1 + 7.9C}\right) \tag{16}$$

3) Because of the equilibrium

$$NH_3 + HCO_3 \rightleftharpoons NH_2COO^- + H_2O$$

$$K_2 = \frac{(NH_2COO^-)}{(NH_3)(HCO_3^-)} = \exp\left(\frac{2000}{T} - 5.6\right) \tag{17}$$

4) Because of the equilibrium

$$NH_3 + HCO_3^- \rightleftharpoons NH_4^+ + CO_3^=$$

$$K_3 = \frac{(NH_4^+)(CO_3^=)}{(NH_3)(HCO_3^-)} = \exp\left(\frac{4750}{T} - 18.16\right) \qquad (18)$$

5) To maintain ionic balance

$$(NH_4^+) = (HCO_3^-) + 2(CO_3^=) + (NH_2COO^-) \qquad (19)$$

The procedure is as follows:

1) Calculate (NH_3) from Equation (17). Since the maximum value of (NH_3) used in this work is about 0.58, the maximum value of $10^{0.025(NH_3)}$ is 1.03. A very good approximation for (NH_3) is

$$(NH_3) = \frac{H_0 P_{NH_3}}{0.0193} 10^{-x} \qquad (20)$$

where

$$x = \frac{0.025\ H_0 P_{NH_3}}{0.0193}$$

A better approximation by trial and error is not needed.

2) Find a first approximation for (HCO_3^-). As a first approximation assume

$$(NH_4^+) = (HCO_3^-)$$

Then, from (15)

$$(HCO_3^-) = \left(\frac{K_1 (NH_3) P_{CO_2}}{0.0133}\right)^{1/2} \qquad (21)$$

Since most of carbon dioxide is in the form of bicarbonate, K_1 can be approximated as

$$K_1 = \exp\left(\frac{7840}{T} - 26.7 + \frac{12.4(HCO_3^-)}{1 + 7.9(HCO_3^-)}\right)$$

First calculate K_1 with $(HCO_3^-) = 0$. Then calculate (HCO_3^-) from (21). Then recalculate K_1 and recalculate (HCO_3^-) and so on until two successive approximations for (HCO_3^-) agree within 0.2 percent.

3) From (17) calculate (NH_2COO^-).

4) Equations (18) and (19) can be combined to eliminate (NH_4^+) and give a quadratic equation for $(CO_3^=)$.

$$2(CO_3^=)^2 + (CO_3^=)\left((HCO_3^-) + (NH_2COO^-)\right)$$
$$- K_3(NH_3)(HCO_3^-) = 0 \qquad (22)$$

Solve (20) for $(CO_3^=)$.

5) Solve (18) or (19) for (NH_4^+).

6) Solve (12) for C.

7) Solve (16) for K_1.

8) Return to (21) and solve for (HCO_3^-).

9) Repeat steps 3 to 8 for successively better approximations of (HCO_3^-).

10) When (HCO_3^-) is know within 0.2 percent, determine A and C from (11) and (12).

16.4 VAPOR-LIQUID EQUILIBRIUM FOR NH_3-H_2S-H_2O

Equilibrium data in graphical form have been published by Beychok.[4] Similar graphs were prepared for the mixture NH_3-CO_2-H_2O. Examination of the two sets of graphs shows that CO_2 is sufficiently volatile compared to NH_3 for the deacidification column to work, that is, for CO_2 to go overhead while holding NH_3 in the bottoms. However, H_2S seems not to be sufficiently volatile compared to NH_3 to be separated in this way and it is doubtful if the all-distillation procedure, as shown in Figure 16-2, will work for the mixture NH_3-H_2S-H_2O. Equilibrium calculations were not made for the four component mixture NH_3-CO_2-H_2S-H_2O, but if CO_2 is present in large excess over H_2S, then H_2S would be expected to go overhead with CO_2. This is because CO_2 is a stronger acid than H_2S. The use of deacidification towers in Lurgi process plants substantiates this supposition.

In fact the Phosam-W process and not the all-distillation process has been used. For costing purposes it was necessary to be sure that a simple stripping column would work with the same steam rate for NH_3-H_2S-H_2O as for NH_3-CO_2-H_2O. It was found that two extra theoretical trays were used when H_2S was the acid gas. The analytical procedure used for the vapor-liquid equilibrium calculations for NH_3-H_2S-H_2O is given below, derived from References 4 and 5.

The only species present are HS^-, NH_4^+, NH_3 and very small concentrations of H_2S, so the calculation is very much simpler than for ammonia and carbon dioxide. The relationships are:

$$P_{H_2S} \text{ (psia)} = 0.0193 \frac{S^2}{(A-S)K_4} \tag{23}$$

$$P_{NH_3} \text{ (psia)} = 0.0193 \frac{A-S}{H_0} 10^{0.025(A-S)} \tag{24}$$

where

A = total ammonia in solution, gm-mole/l

S = total hydrogen sulfide in solution, gm-mole/l

As before

$$H_0 = \exp\left(\frac{4150}{T} - 16.54\right) \tag{14}$$

K_4 is given by the equations

$$\frac{1}{K_4} = 10^{a-0.089S} \qquad (25)$$

where

$$a = \frac{(t°C)^{0.627}}{5.95} \qquad (26)$$

(Note that Equation (8) of Reference 4 seems to be misprinted in that the number 0.089 is missing. The above equations do give the vapor pressures given on the graphs in Reference 4.)

To calculate the liquid composition from the vapor pressures, the procedure is:

1) The first approximation to A-S is

$$(A-S)_1 = \frac{H_a P_{NH_3}}{0.0193} \, 10^{-(0.025 H_a P_{NH_3})/0.0193}$$

The second approximation is

$$(A-S)_2 = \frac{H_a P_{NH_3}}{0.0193} \, 10^{-0.025(A-S)_1}$$

and so on.

2) With A-S established, calculate S from

$$S = \left(\frac{K_4 (A-S) P_{H_2S}}{0.0193} \right)^{\frac{1}{2}}$$

For the first approximation use

$$K_4 = 10^{-a}$$

For the second approximation use

$$K_4 = 10^{-a+0.089S_1}$$

and so on.

16.5 DEACIDIFICATION COLUMNS FOR NH_3-CO_2-H_2O

The basis for all calculations is F = 100 moles/hr water in feed. The following feed solutions were studied.

Feed concentrations (mg/l)		Feed rates (moles/hr)		
NH_3	CO_2	NH_3 (FN)	CO_2 (FC)	FC/FN
8,000	15,500	0.848	0.636	0.75
4,000	7,800	0.424	0.318	0.75
4,000	3,900	0.424	0.159	0.375

The deacidification tower is a two-variable problem, since the refluxed wash water W and the steam rate S can both be varied. If the steam rate was not high enough it was not possible to strip out CO_2 below the feed, and if the washwater rate was not high enough it was not possible to prevent stripping ammonia out the top. There is a narrow range of wash and steam rates within which the tower will function satisfactorily; steam rates should be in the range 8 to 10 moles/100 moles feed and wash rates in the range 120 to 150 moles/100 moles feed. This high wash rate means that a lot of steam is needed in the ammonia tower reboiler.

Some results are given on Table 16-1. Steam rates of 6, not shown on Table 16-1, do not work. With a steam rate of 8, water rates below 100 do not work.

The feed, in most cases, should be about one half a theoretical stage above the bottom. The system is quite sensitive. If the bottom takeoff is too low, the ammonia concentration is too low; if the bottom takeoff is not low enough, the carbon dioxide concentration is too high. With a feed in which the molar ratio $(CO_2)/(NH_3)$ is 0.75, it is not possible to get less than 10 to 15 percent of the feed carbon dioxide out the bottom. With feed in which the molar ratio $(CO_2)/(NH_3)$ is 0.375, we cannot get less than 20 to 25 percent of the feed carbon dioxide out the bottom. There was no problem getting only 1 percent of the feed ammonia out the top, and altering this to 2, 4 or 6 percent made little difference. It may be possible to inject some

TABLE II.1. DEACIDIFICATION TOWER FOR [illegible]

Basis 10% mole water in feed.

F (moles/hr)	F' (moles/hr)	[illegible] (% [illegible])	[illegible] (% [illegible])	[illegible] (moles/hr)	W (moles/hr)	Feed Stage	Bottom Stage No.	Bottom Stage [illegible] (% [illegible])	Bottom Stage [illegible] (% [illegible])
0.424	0.319	1	99	10	150	12	[illegible]	[illegible]	[illegible]
					140	15	[illegible]	[illegible]	[illegible]
					120	5	[illegible]	[illegible]	[illegible]
				8	150	7	[illegible]	[illegible]	[illegible]
					140	8	[illegible]	[illegible]	[illegible]
					120	11	[illegible]	[illegible]	[illegible]
					100	8	[illegible]	[illegible]	[illegible]
			95	8	150	7	[illegible]	[illegible]	[illegible]
					140	8	[illegible]	[illegible]	[illegible]
					130	9	[illegible]	[illegible]	[illegible]
					120	11	[illegible]	[illegible]	[illegible]
			90	8	150	7	[illegible]	[illegible]	[illegible]
					140	8	[illegible]	[illegible]	[illegible]
					130	9	[illegible]	[illegible]	[illegible]
					120	11	[illegible]	[illegible]	[illegible]
		2	99	8	150	5	[illegible]	[illegible]	[illegible]
					140	7	[illegible]	[illegible]	[illegible]
					120	10	[illegible]	[illegible]	[illegible]
		3	99	8	150	5	[illegible]	[illegible]	[illegible]
					140	6	[illegible]	[illegible]	[illegible]
					120	8	[illegible]	[illegible]	[illegible]
		6	99	8	150	5	[illegible]	[illegible]	[illegible]
					140	5	[illegible]	[illegible]	[illegible]
					120	7	[illegible]	[illegible]	[illegible]
0.424	0.319	2	95	8	150	6	[illegible]	[illegible]	[illegible]
					140	7	[illegible]	[illegible]	[illegible]
					120	10	[illegible]	[illegible]	[illegible]
		4	95	8	150	5	[illegible]	[illegible]	[illegible]
					140	6	[illegible]	[illegible]	[illegible]
					130	8	[illegible]	[illegible]	[illegible]
		5	95	8	150	5	[illegible]	[illegible]	[illegible]
					140	[illegible]	[illegible]	[illegible]	[illegible]
					130	6	[illegible]	[illegible]	[illegible]
					120	7	[illegible]	[illegible]	[illegible]
		6	95	8	150	5	[illegible]	[illegible]	[illegible]
					140	5	[illegible]	[illegible]	[illegible]
					120	7	[illegible]	[illegible]	[illegible]

---

*Not workable

(continued)

TABLE [illegible] (continued)

[illegible]

wash into the lower part of the column as a control.

The tower height increases as the wash rate is decreased from 150 to 120 and as the fraction of ammonia out of the top is decreased. The extreme range of variation is from 7 to 12 theoretical stages. Doubling the feed concentration has little effect.

For cost estimating, S = 8 lb steam/100 lb feed, a wash (reflux) rate of 130 lb water/100 lb feed; 12 theoretical trays (24 actual trays[3]) above the feed and 1 theoretical tray (2 actual trays[3]) below the feed were assumed.

16.6 AMMONIA CONCENTRATION

Aqueous ammonia leaves the bottom of the deacidification tower at less than half its strength in the feed water and must be concentrated. The ammonia tower calculations involve only two components and were made using the methods given in standard chemical engineering texts. Vapor-liquid equilibrium data were taken from Reference 6 at 65 psia total pressure. For most of the tower the concentration is so low that Henry's law applies, and it was used in the form

$$p_{NH_3} \text{ (psia)} = 0.0193\ A/H_D$$

where, as before,

$$H_D = \exp\left(\frac{4150}{T} - 16.54\right)$$

At 65 psia and 300°F (422°K) this becomes

$$x = 0.074y$$

where

x = mole fraction NH_3 in liquid
y = mole fraction NH_3 in vapor

The top concentration was set at 30 wt percent ammonia and 99 percent of the feed ammonia was sent out the top. The tower height was not sensitive to feed concentration in the range 4,000 to 2,000 mg/l. The results are shown on Figure 16-6. For cost estimating, .13 lb steam/lb feed and 11 theoretical stages (22 actual stages[3]) with 2 above the feed and 9 below the feed were used. It must be remembered that for every 100 lb water treated, about 227 lb are fed to the ammonia tower, so the steam rate is 29 lb steam/100 lb dirty water treated, which is high.

16.7 PHOSAM-W PROCESS

In this section the Phosam-W process as shown in Figure 16-1 is briefly described.

The process was developed to remove the free ammonia from waste water streams containing both ammonia and acid gases such as H_2S, CO_2 and HCN. Traditionally this was accomplished by stripping from the vapor with sulfuric acid to produce ammonium sulfate crystals. By substituting phosphoric acid for sulfuric acid, a cyclic process is possible for producing anhydrous ammonia. The basic concept behind the process is that phosphoric acid has three hydrogen atoms that can be replaced by ammonium ions in water solution. Therefore there should exist a range of mole ratios, ammonia to phosphoric acid, over which the ammonia is bound tightly enough for good absorption but still loosely enough so that it can be stripped back out.

As can be seen in the flow diagram, the process consists of three main pieces of equipment: the superstill, which is a stripper and absorber, a Phosam stripper and a fractionator. The liquid feed stream containing acid gases and ammonia is divided into two streams which are preheated and then recombined, at the bubble point, to enter the top of the stripping section of the superstill. Both the ammonia and acid gases are stripped from the water at an operating pressure of 4 psig.

The stripped water leaves the bottom of the superstill containing less than 200 ppm free NH_3 and is used for heating part of the feed stream in the feed preheater. Boilup for the superstill stripper is provided primarily by indirect steam at 60 psig. Direct flashing of the fractionator bottoms in

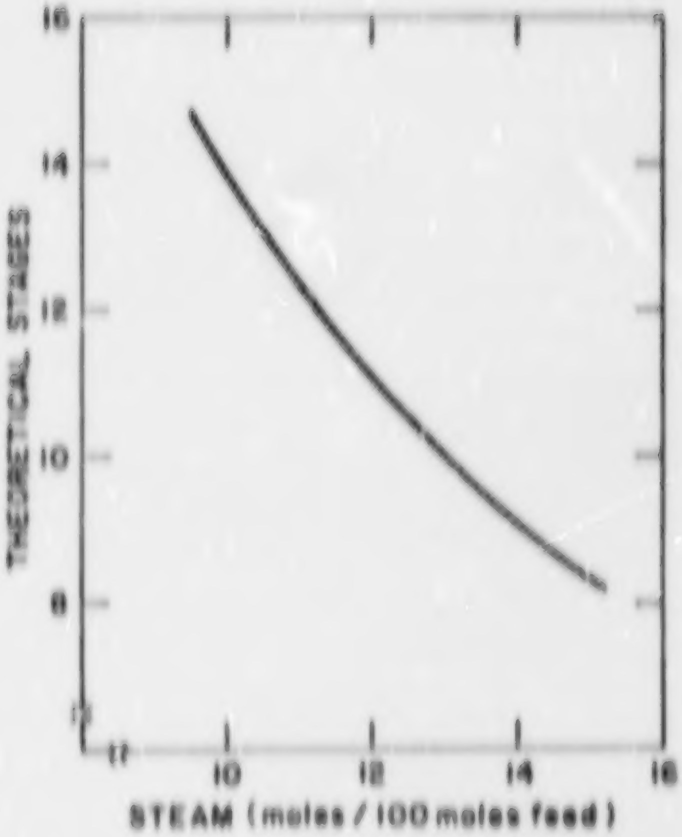

Figure 16-6. Ammonia tower.

the superstill stripper provides the remaining reboiler duty.

The vapor containing the stripped ammonia and acid gases passes upward into the absorber section of the superstill. In the bottom stage of the absorber, it is contacted with an intense spray of ammonium phosphate solution which has been cooled in an external air-cooled exchanger. The vapors then pass into a tray section where they are further scrubbed by the lean ammonium phosphate solution in counter-current contact. The vapors then leave the top of the absorber at a pressure of 3 psig.

The net flow of rich solution from the absorber is purged of acid gases by vapors generated in a solution exchanger in a contactor compartment at the bottom of the absorber. The rich solution is then pumped from the absorber to the stripper, after passing through the upper section of the stripper condenser where it is heated by exchange with the overhead vapors from the stripper.

The stripper is operated at elevated pressure. This is because the stripping equilibrium is markedly improved at high pressures. A high operating pressure in the stripper reduces the steam requirements. The function of the stripper is to remove NH_3 from the rich solution to regenerate the lean solution for recycle to the tray section of the absorber. Boilup in the stripper is provided by steam at 600 psig in the stripper reboiler. The hot, lean solution leaving the stripper bottom is cooled and enters the top of the superstill absorber section.

The aqua ammonia vapor, 10 to 20 wt percent ammonia, from the top of the stripper passes through a two-stage condenser. The top stage cools and condenses part of the vapor, thus recovering much of its heat content. In the bottom section the remaining vapor is totally condensed by heat exchange with cooling water. The condensate flows to the fractionator feed tank where it is pumped into the ammonia fractionator column. In the fractionator the aqua ammonia is distilled, at elevated pressure, into 99.99 percent pure ammonia leaving the top and less than 0.05 percent ammonia leaving the bottom.

The overhead pure ammonia vapor is condensed in the fractionator condenser by heat exchange with cooling water. Reflux is returned to the top of the column.

By the addition of a very small flow of sodium hydroxide solution at the proper location, traces of acid gases and organic compounds are prevented from accumulating in the fractionator and eventually contaminating the product.

The slightly alkaline, pressurized hot water from the bottom of the tower is flashed directly into the bottom of the superstill providing a portion of the steam requirement.

16.8 EQUIPMENT SIZE AND CAPITAL COST

For the equipment shown on Figure 16-2, the size and cost for the all-distillation procedure have been estimated. The column diameters were estimated using the Glitsch manual.[7] The costs were taken from Guthrie,[8] using the multipliers given by him for erection and for stainless steel (or cladding) and multiplying by 1.68 to update the costs to early 1976. The results are given on Table 16-2 and plotted on Figure 16-3.

Equipment sizes for the Phosam-W process were provided by United States Steel Engineers and Consultants, and the capital cost was estimated similarly to the all-distillation process with the results shown on Table 16-3 and Figure 16-3.

For the SRC plant where the separation is between NH_3, H_2S and water, the size and cost for the Phosam-W plant is shown on Table 15-4 and Figure 16-3. The equipment size provided by United States Steel Engineers and Consultants, as reproduced in Table 16-4, was for a coal liquefaction process, not SRC but similar.

16.9 OPERATING COST AND ENERGY

The all-distillation procedure uses about 2.9×10^6 Btu/thousand gallons. This high energy need is caused by the large recycle to the deacidification tower necessitating large amounts of steam in the ammonia tower reboiler. The Phosam-W process uses about 1.7×10^6 Btu/thousand gallons and is cheaper than the all-distillation process. Phosam-W is the process of choice. Operating costs are presented on Table 16-5 and Figure 16-4 for gas plants. For SRC plants the capital is a little higher, and this is reflected in Figure 16-4.

TABLE 16-2. COSTS FOR AMMONIA SEPARATION BY ALL-DISTILLATION PROCESS

(Material S.S. clad, 24" tray spacing)

Throughput, 10^6 gal/day	0.5	1.5	3.0	4.5
Deacidification column:				
Number of columns	1	1	1	2
Top: ht, ft	55	55	55	
dia, ft	6.0	10.0	13.8	
Bottom: ht, ft	25	25	25	
dia, ft	7.5	12.0	16.6	
Reboiler, ft^2	1,555	4,667	9,222	
Cost, 10^6\$	0.78	1.4	2.5	3.8
Ammonia Tower:				
Number of columns	1	1	2	3
Top: ht, ft	15	15	15	
dia, ft	6.5	11.0	11.0	
Bottom: ht, ft	40	40	40	
dia, ft	8.5	14.0	14.0	
Reboiler, ft^2	5,354	16,069	32,141	
Air cooler, ft^2	7,902	23,705	47,410	
Cost, 10^6\$	1.1	2.4	4.9	7.3
Total Equipment Cost* 10^6\$	1.9	3.8	7.4	11.1

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*Royalty and engineering not included

TABLE 16-1. SIZE AND COST OF PHOSAM-W PROCESS IN A GAS PLANT

(Material S.S. clad)

Throughput, 10^6 gal/day	4.5
Equipment	
Superstill	
Top: ht, ft	62
dia, ft	11.5
Bottom: ht, ft	69
dia, ft	15.5
Exchangers	
E-1, ft^2	7,000
E-2, ft^2	120
E-6, ft^2	7,330
E-7, ft^2	8,270
E-8, ft^2	29,690
Cost, 10^6\$	5.1
Phosam Stripper	
ht, ft	67
dia, ft	7.0
Exchangers	
E-3: top, ft^2	5,940
bottom, ft^2	1,360
E-9, ft^2	3,140
Cost, 10^6\$	1.1
Fractionator	
ht, ft	64.00
dia, ft	3.25
Exchangers	
E-5, ft^2	2,810
E-10, ft^2	930
Cost, 10^6\$	0.69
Approx. royalty 10^6\$	1.1
Total Equipment & Royalty Cost, 10^6\$	8.0

TABLE 16-4. SIZE AND COST OF PHOSAM-W PROCESS IN SRC PLANT

(Material S.S. clad)

Throughput, 10^6 gal/day	1.6
Equipment	
Superstill	
Top: ht, ft	84
dia, ft	14.5
Bottom: ht, ft	61
dia, ft	9.5
Exchangers	
E-1, ft^2	12,000
E-2, ft^2	540
E-6, ft^2	6,725
E-7, ft^2	11,300
E-8, ft^2	5,100
Cost, $10^6$$	4.2
Phosam Stripper	
ht, ft	70
dia, ft	9.5
Exchangers	
E-3: top, ft^2	8,600
bottom, ft^2	1,760
E-9, ft^2	5,440
Cost, $10^6$$	1.7
Fractionator	
ht, ft	65
dia, ft	5.25
Exchangers	
E-5, ft^2	7,100
E-10, ft^2	2,020
Cost, $10^6$$	1.3
Approx. royalty, $10^6$$	1.0
Total Equipment & Royalty Cost, $10^6$$	8.2

TABLE 11-5. OPERATING COSTS FOR AMMONIA SEPARATION IN GAS PLANTS

Throughput, 10^6 gals/day	0.5	1.5	3.0	4.5
	Costs ($/thousand gallons)			
Capital charges including maintenance at 17%/yr (330 days/yr):	1.41	0.95	0.91	0.92
Energy at $1.00/10^6 Btu	3.06	3.06	3.06	3.06
Caustic soda	0.04	0.04	0.04	0.04
Phosphoric acid	0.01	0.01	0.01	0.01
	4.52	4.06	4.02	4.03

*Sale of ammonia at $140/ton[9] with 95% recover yields $3.30/10^3 gallons of water treated when feed water contains 6,000 mg/l ammonia, or generally $0.55/(10^3 gallons)(1,000 mg ammonia/l).

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SECTION 17

SOLVENT EXTRACTION OF PHENOL

17.1 INTRODUCTION AND SUMMARY OF RESULTS

Phenol can be extracted from dirty process condensate and a crude, mixed product recovered for sale. Alternatively phenol can be destroyed by biological treatment. In this section is given a simplified procedure for determining the cost of solvent extraction so as to determine when, and whether, it should be used.

Solvent extraction is standard for all Lurgi process plants where the proprietary Phenosolvan process is used. The Phenosolvan process has been described:[1] "The liquid is mixed with an organic solvent (isopropyl ether) in an extractor in order to dissolve the phenol. The phenol solvent mixture is collected and fed to solvent distillation columns where crude phenol is recovered as the bottom product and the solvent as the overhead product. The solvent is then recycled to extractors after removing some of the contained water. The raffinate is stripped with fuel gas to remove traces of solvent which are picked up in the extraction step. The fuel gas is scrubbed with crude phenol product to recover the solvent. Finally, the phenol solvent mixture is distilled in the solvent recovery stripper to produce the crude phenol product, and the solvent is recycled to the extraction step. The solvent free raffinate is heated and steam stripped to remove carbon dioxide, hydrogen sulfide, and ammonia."

This scheme is illustrated on Figure 17-1, which is also partly taken from Reference 2. For the discussion in this section we have not designed the full distillation section but have idealized the situation to that of Figure 17-2. This means that the cost estimates are low.

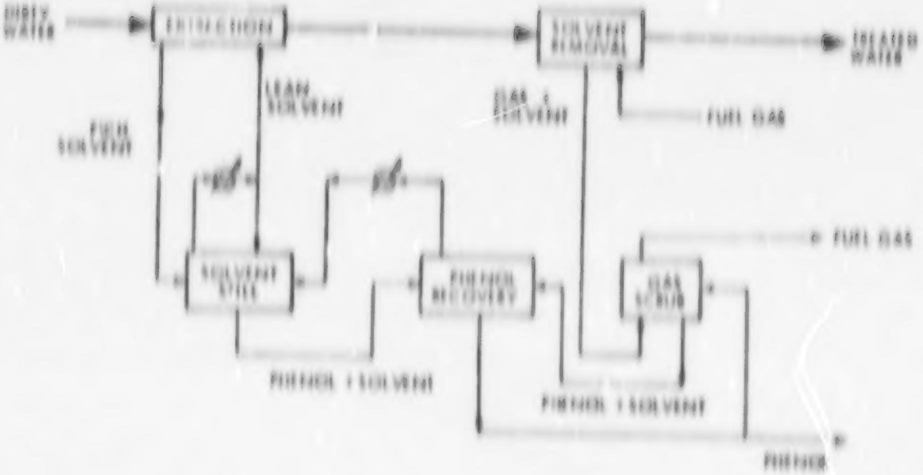

DIRTY WATER
EXTRACTION
SOLVENT REMOVAL
TREATED WATER
LEAN SOLVENT
RICH SOLVENT
GAS & SOLVENT
FUEL GAS
FUEL GAS
SOLVENT STILL
PHENOL RECOVERY
GAS SCRUB
PHENOL + SOLVENT
PHENOL + SOLVENT
PHENOL

Figure 17-1. Phenosolvan process.

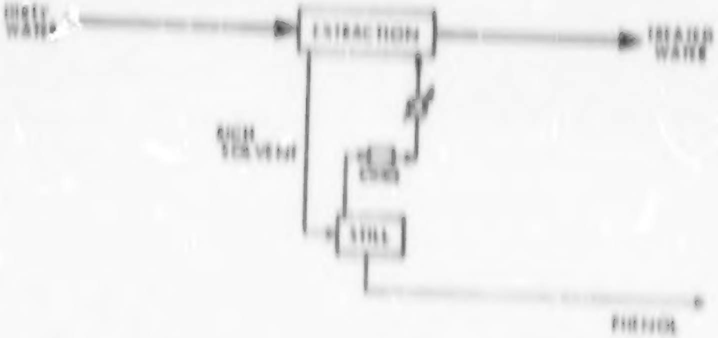

DIRTY WATER
EXTRACTION
TREATED WATER
RICH SOLVENT
COND
STILL
PHENOL

Figure 17-2. Idealized solvent extraction.

To determine cost, an optimization procedure is necessary. The more solvent that is circulated, the smaller the extraction equipment becomes and the larger the still becomes. There is an optimum solvent circulation rate. In Sections 17.2 to 17.4 some minimum costs have been found and these are given on Table 17-1 for the case of benzene as the solvent.

If 95 percent of the phenol is extracted, the minimum possible cost is 2.9×10^6 \$/yr to treat 10^6 lb water/hr. This is about \$3/thousand gallons and is not cheap. Furthermore, extraction is not necessary so will only be done if it pays for itself. Two things offset the cost of extraction: reduced cost of downstream biological treatment and income from the phenol sold.

Refined phenol sells for about 26¢/lb so the crude mixture extracted from waste water is probaly not worth more than 6¢/lb. Values as low as 1.7¢ to 2.2¢/lb have been suggested.[3,6] As a fuel phenol has a higher heating value of 11,380 Btu/lb and might be worth 2.3¢/lb at \$2/10^6 Btu.

We have very little information on the nature of the non-phenolic biochemical oxygen demand and cannot estimate with accuracy the reduced cost of biological treatment resulting when phenol is extracted. Referring briefly to Section 18, the cost of biotreatment is very much dependent on the BOD removal rate. If phenol is extracted and the BOD is reduced to about half, the cost of biotreatment may be reduced by about one third; that is, about \$1/thousand gallons treated may be saved on biotreatment. In Lurgi process there is some possibility that the water, after extraction and ammonia separation, can be used as cooling water makeup without any biotreatment at all. In this study this has not been assumed possible.

The lowest cost shown on Table 17-1 is \$$2.9 \times 10^6$/yr to recover 45.6×10^6 lb phenol/yr with 95 percent recovery from a feed of 1000 lb/hr (2.88×10^6 gal/day) having 6000 mg/l phenol. If 0.9×10^6 \$/yr are saved by reduced need for downstream biological treatment the extraction will break even even if phenol can be sold for 4.4¢/lb. However, the cost estimates may be low.

Some conclusions can be drawn. Extracting more than 95 percent of phenol in the feed water is unlikely to be worthwhile. A feed concentration of more than 6000 ppm phenol is probably required before extraction pays. A better

TABLE 17-1. PHENOL RECOVERY

Basis: 10^6 lb water/hr; benzene solvent (K = 2.3)

(The breakeven value of phenol is the minimum cost divided by the quantity of phenol recovered.)

Feed phenol (ppm)	% Phenol Recovered	Phenol Recovered (10^6 lb/yr)	Min. cost (10^6 $/yr)	Breakeven value of phenol ¢/lb
6000	99.8	47.9	4.18	8.7
6000	99	47.5	3.62	7.6
6000	95	45.6	2.90	6.4
2000	99.8	16.0	4.18	26
2000	99	15.8	3.62	23
2000	95	15.2	2.90	19
600	99.8	4.8	4.18	87
600	99	4.8	3.62	75
600	95	4.6	2.90	63

solvent than benzene would increase the usefulness of extraction. Solvent extraction requires quite a lot of energy. For example, using 0.7 lb solvent/lb water where the solvent has a latent heat of 170 Btu/lb, then the energy required is about 1×10^6 Btu/thousand gallons of water treated.

Solvent extraction removes most of the volatile organic contaminants in foul condensate. Extraction is a prerequisite to purifying the water by distillation. Extraction will assist the separation of ammonia.

In the treatment plants designed for this study, solvent extraction has not been considered except where distillation has been considered. This is most probably correct for Hygas, probably correct for Synthane, marginal for the Lurgi process used in the power plants, and should be studied further and possibly reconsidered for the Solvent Refined Coal plant.

Section 17.5 describes an adsorption process for phenol, as yet untested, which has a strong potential for use in the future. At the present time the cost seems to be comparable to solvent extraction, but the adsorption process is new and still undergoing improvements. In any situation where solvent extraction is considered, adsorption systems should also be investigated.

17.2 SIMPLE EXTRACTION EQUATION

Consider a simplified, ideal, counter-current extraction using the nomenclature of Figure 17-3. Complete immiscibility of solvent and water is assumed, and at the exit of each theoretical stage it is assumed that

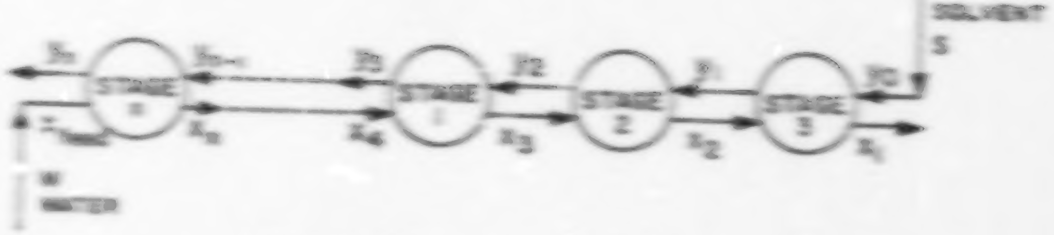
$$\frac{y_n}{x_n} = k \quad \text{(a constant)} \tag{1}$$

Material balances for the solute (phenol) give

Stage 1

$$s(y_1 - y_0) = s(x_1 - y_0) = w(x_2 - x_1)$$

$$x_2 = \frac{sk}{w} x_1 + x_1 - sy_0$$


SOLVENT
S
y_0
y_1
y_2
y_3
y_{n-1}
y_n
STAGE 3
STAGE 2
STAGE 1
STAGE n
x_1
x_2
x_3
x_4
x_n
x_{feed}
W
WATER

w = water feed rate, 10^6 lb/hr

s = solvent feed rate, 10^6 lb/hr

y = phenol concentration in solvent, ppm

x = phenol concentration in water, ppm

Figure 17-1. Ideal counter-current liquid-liquid extraction.

$$\frac{x_2}{x_1} = \frac{sk}{w} + 1 - \frac{sy_0}{x_1}$$

Stage 2

$$\begin{aligned} s(y_2 - y_1) &= sk(x_2 - x_1) \\ &= sk\left(\frac{skx_1}{w} - sy_0\right) = w(x_3 - x_2) \\ &= w\left(x_3 - \frac{skx_1}{w} - x_1 + sy_0\right) \end{aligned}$$

$$\begin{aligned} x_3 &= \frac{sk}{w}\left(\frac{skx_1}{w} - sy_0\right) + \frac{skx_1}{w} + x_1 - sy_0 \\ &= \left(\frac{sk}{w}\right)^2 x_1 + \frac{sk}{w} x_1 + x_1 - sy_0\left(\frac{sk}{w} + 1\right) \end{aligned}$$

Now taking y_0 , the concentration of phenol in the feed solvent, to be negligible, one obtains

Stage n

$$\frac{x_f}{x_1} = \left(\frac{sk}{w}\right)^n + \ldots + \frac{sk}{w} + 1$$

so

$$\frac{sk}{w}\frac{x_f}{x_1} = \left(\frac{sk}{w}\right)^{n+1} + \ldots + \left(\frac{sk}{w}\right)^2 + \frac{sk}{w}$$

and, by subtraction,

$$\frac{x_f}{x_1} = \frac{\left(\frac{sk}{w}\right)^{n+1} - 1}{\frac{sk}{w} - 1} \qquad (2)$$

or

$$\frac{\log\left[\left(\frac{x_f}{x_1}\right)\left(\frac{sk}{w} - 1\right) + 1\right]}{\log\left(\frac{sk}{w}\right)} = n + 1 \qquad (3)$$

Equation (3) relates the number of stages n to the desired extraction ratio x_f/x_1, the extractive ability of the solvent k and the flow rate ratio of solvent to water s/w. Figure 17-4 is a graphical representation of Equation (3). For a chosen situation in which x_f/x_1, w and k are fixed, the number of stages n can be decreased by increasing the solvent rate s. With fewer stages the extraction column can be smaller and costs less. However, all of the solvent has to be evaporated to separate it from the phenol, and increasing the solvent rate increases the boiler and energy cost. To find the cost of solvent extraction the design must be optimized. To do the optimization one first finds the cost for a particular example, called the base case, and then scales from this case to do the optimization. A related technique is described by Scheibel.[4]

17.3 BASE CASE EXAMPLE

The base case example has been arbitrarily chosen as:

(1) Benzene to be the solvent because information is published: k = 2.3 and the latent heat of vaporization = 170 Btu/lb.

(2) x_f/x_1 = 100 (99 percent extracted).

(3) w = 1 (i.e., 10^6 lb/hr) and s = 1.3 (i.e., 1.3 × 10^6 lb/hr), so sk/w = 2.99.

The number of stages is then n = 3.8.

Otto H. York Co., Parsippany, N.J. has kindly supplied a basis for estimating an erected cost of Scheibel extraction columns. The system will use 10 columns, each 60-70 ft high and 10 ft in diameter in type 304 SS. Each column has a 30 hp agitator, total (for 8,000 hrs/yr) 1.79 × 10^6 kw-hrs/yr. The water flow is about 20 ft/hr and the solvent flow is about 30 ft/hr. The

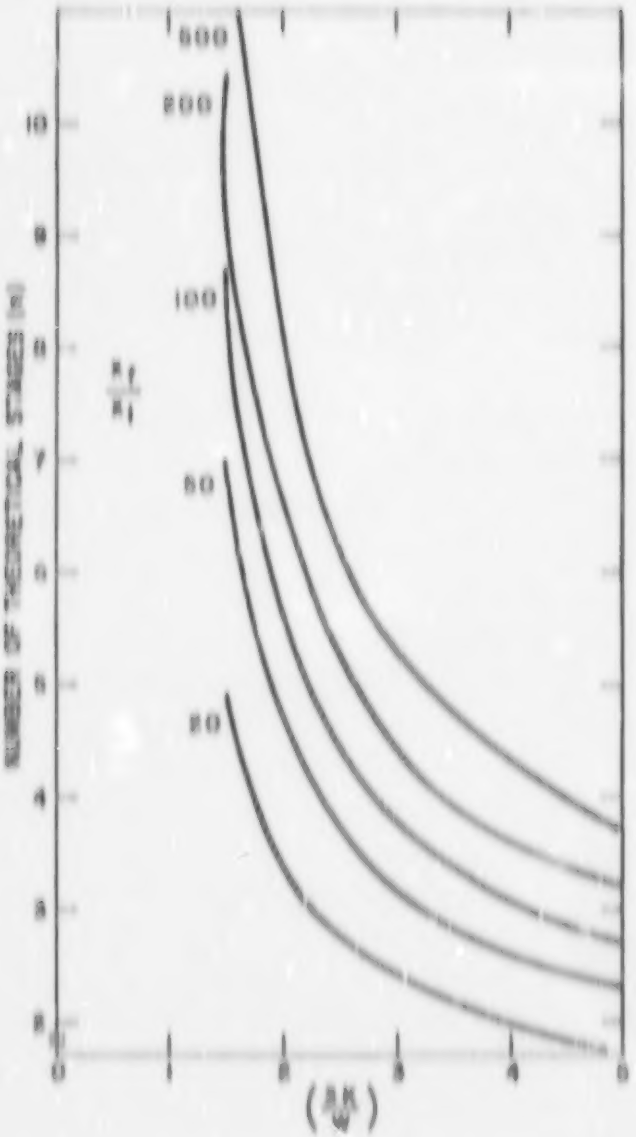


Figure 17-4. Extraction equation.

columns cost \$3.75 × 10^6. A charge of 17%/yr of capital has been taken for amortization, maintenance and other capital related items. The annual charge for the extraction columns is \$0.64 × 10^6/yr. The agitator energy at 2¢/kw-hr costs \$0.036 × 10^6/yr.

The benzene used as a solvent must be distilled from the extracted phenol. Distillation requires a reboiler with a steam feed and a condenser. The boiler is assumed to operate at about 16 psia so that the condenser can be air cooled and condensed at 180°F. The condensed solvent will then have to be further cooled to about 100°F in a water cooled heat exchanger. For a first approximation, no distillation trays have been provided and no reflux. This is shown in Figure 17-2. The load on the boiler to heat the benzene from 100 to 180°F and then to vaporize it is about (210 Btu/lb)(1.3 × 10^6 lb/hr) = 273 × 10^6 Btu/hr. The load on the air cooled condenser is about (170 Btu/lb)(1.3 × 10^6 lb/hr) = 221 × 10^6 Btu/hr, and the load on the water cooled solvent cooler is about (40 Btu/lb)(1.3 × 10^6 lb/hr) = 52 × 10^6 Btu/hr. For the boiler, the coefficient is 150 Btu/(hr)(ft^2)(°F) (based on about 200 on the boiling benzene side and 1000 on the condensing steam side) and ΔT = 74°F. The boiler requires 25,000 ft^2 and costs \$1.4 × 10^6. For the air cooled condenser, the coefficient is taken to be 50 Btu/(hr)(ft^2)(°F) and ΔT = 88°F. The condenser requires 50,000 ft^2 and costs \$1.8 × 10^6. For the solvent cooler, the coefficient is taken to be 80 Btu/(hr)(ft^2)(°F) and ΔT = 50°F. The solvent cooler requires 13,000 ft^2 and costs \$0.73 × 10^6. The total distillation equipment costs \$3.9 × 10^6. At 17%/yr the annual charge is \$0.66 × 10^6/yr.

The air cooled condenser requires a fan of 750 kw costing 0.12 × 10^6 \$/yr to operate. If low pressure steam to the boiler is taken at \$1.80/10^6 Btu, the steam costs are \$3.93 × 10^6/yr.

In sum, the base case annual charges are

		10^6 \$/yr
Extractors:	capital	0.64
	energy	0.04
Distillation:	capital	0.66
	energy	4.05

17.4 OPTIMIZATION

The extractor cost will depend, but not linearly, on the height of the columns which in turn depends on the number of theoretical stages n and on some combination of the number of columns and their diameter which in turn depends on the throughput measured as (s+w). In the narrow range of interest, the cost for case "i" can be related to the cost for the base case "b" by the equation

$$\frac{\text{cost (i)}}{\text{cost (b)}} = \left(\frac{s_i + w_i}{s_b + w_b}\right)^{0.5} \frac{n_i}{n_b} \qquad (4)$$

For optimization calculations take $w_i = w_b = 1$ (i.e., 10^6 lb/hr of water) so Equation (4) becomes

$$\text{cost of extractors} = 0.68 \times 10^6 \left(\frac{s + 1}{2.3}\right)^{0.5} \frac{n}{3.8}$$

$$= 0.116 \times 10^6 \ (s + 1)^{0.5} n \ \ \$/\text{yr} \qquad (5)$$

The distillation costs are proportional to the solvent rate s and are

$$\text{cost of distillation} = 4.71 \times 10^6 \ \frac{s}{1.3}$$

$$= 3.62 \times 10^6 \ s \ \$/\text{yr} \qquad (6)$$

Equations (3), (5) and (6) are used for optimization.

A sample optimization is shown on Figure 17-5. Figure 17-5 includes the base case, which is clearly a long way from the optimum. The minimum is clear and readily determinable. Additional results are given on Table 17-2 as a function of the percent of the feed phenol extracted. The calculations were also made for better solvents than benzene (for which k = 2.3). When calculating costs for these imaginary solvents the latent heat of vaporization was kept constant at 170 Btu/lb. In using Table 17-2 it must be

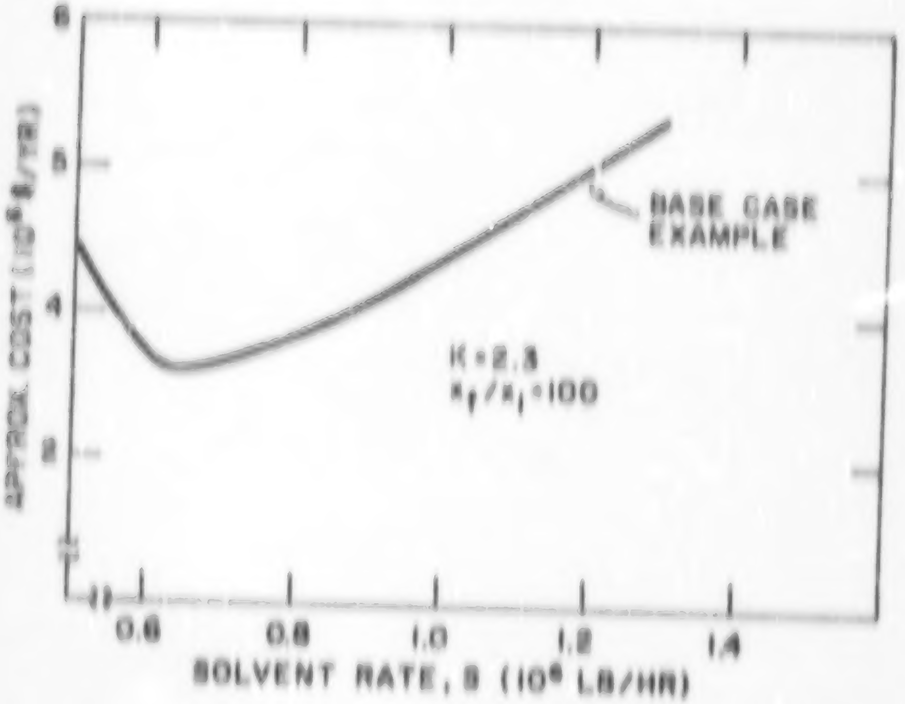


Figure 17-5. Sample optimization.

TABLE 17-2. APPROXIMATE MINIMUM ANNUAL COST OF SOLVENT EXTRACTION FOR AN IDEAL CASE

Basis: 10^6 lb feed water/hr (= w)

% Feed phenol extracted	Extraction ratio, x_f/x_1	Solvent k	Solvent rate, s (10^6 lb/hr)	$\frac{sk}{w}$	No. of stage (n)	Cost 10^6 \$/yr
95	30	2.3	0.5	1.15	8.9	2.90
99	100	2.3	0.65	1.5	8.7	3.62
99.8	500	2.3	0.67	1.58	11.2	4.18
95	20	4	0.35	1.38	5.7	2.02
99	100	4	0.38	1.5	8.7	2.54
95	20	6	0.25	1.5	5.9	1.67
99	100	6	0.33	2.0	5.7	1.95

remembered that the costs apply to an ideal case, that is, to a solvent that is completely immiscible with water and that can be distilled from phenol without reflux. The costs are low.

17.3 SELECTIVE ADSORPTION OF PHENOL

Rohm and Haas Company manufactures synthetic polymeric adsorbents which can accept high loadings of phenol and may be sufficiently selective for phenol that recovered phenol can be sold[5] (the selectivity requires testing). Once phenol is loaded onto the solid, it can be removed by a solvent which need not be immiscible with water. The added choice of solvent gives the possibility of very high concentrations of phenol in the solvent going to distillation with drastic reduction in the energy required for distillation, which is the largest cost.

Without extensive tests a detailed cost estimate is not possible. Rohm and Haas has kindly supplied a "ball park" estimate for complete "grass roots" type of installation to treat 10^6 lb/hr water having 6000 ppm phenol with 9[illegible] percent phenol removal. The systems use either acetone regeneration as pictured in Figure 17-6 or gasoline regeneration as shown in Figure 17-7. To complete the scheme of Figure 17-7, a very simple still used for benzene liquid-liquid extraction has been added. The gasoline rate is 0.0895×10^6 lb/hr. There are 11 adsorption columns each with 950 ft^3 of resin. Six columns are in use at any moment and six are being regenerated. Two columns are spare. The costs are presented on Table 17-3. The costs have been adjusted by using the same unit costs as in the rest of the report. Labor cost has been omitted as in the rest of the report. Table 17-3 also presents the costs for the optimized liquid-liquid extraction system for 99 percent recovery with benzene solvent ($k = 2.3$) (details on Table 17-2; benzene rate 0.65×10^6 lb/hr).

The cost apparently increases as the completeness of the design and sophistication of the estimate increases. For the moment it must be assumed that the systems are comparable. However, the adsorbent systems are very new; the first commercial installation in the United States was started up in 1975, and improvements are to be expected. In any situation where solvent extraction is considered, adsorption systems should also be investigated.

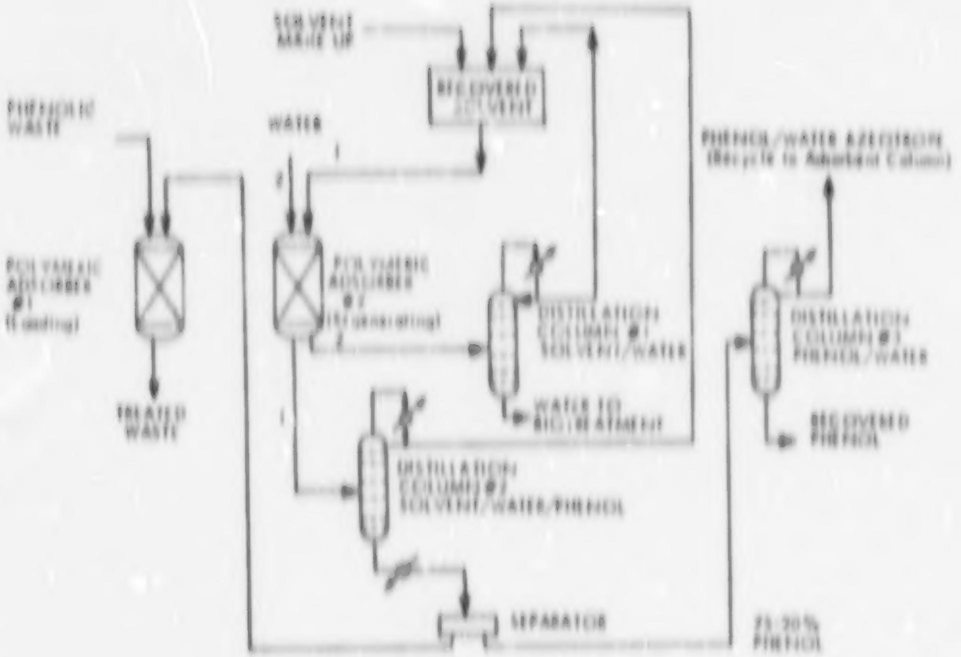

SOLVENT MAKE UP
RECOVERED SOLVENT
PHENOLIC WASTE
WATER
1
2
POLYMERIC ADSORBER #1 (Loading)
POLYMERIC ADSORBER #2 (Regenerating)
TREATED WASTE
2
1
DISTILLATION COLUMN #1 SOLVENT/WATER
WATER TO BIOTREATMENT
DISTILLATION COLUMN #2 SOLVENT/WATER/PHENOL
SEPARATOR
PHENOL/WATER AZEOTROPE (Recycle to Adsorbent Column)
DISTILLATION COLUMN #3 PHENOL/WATER
RECOVERED PHENOL
25-30% PHENOL

Figure 17-6. Phenol recovery by adsorption with acetone regeneration.

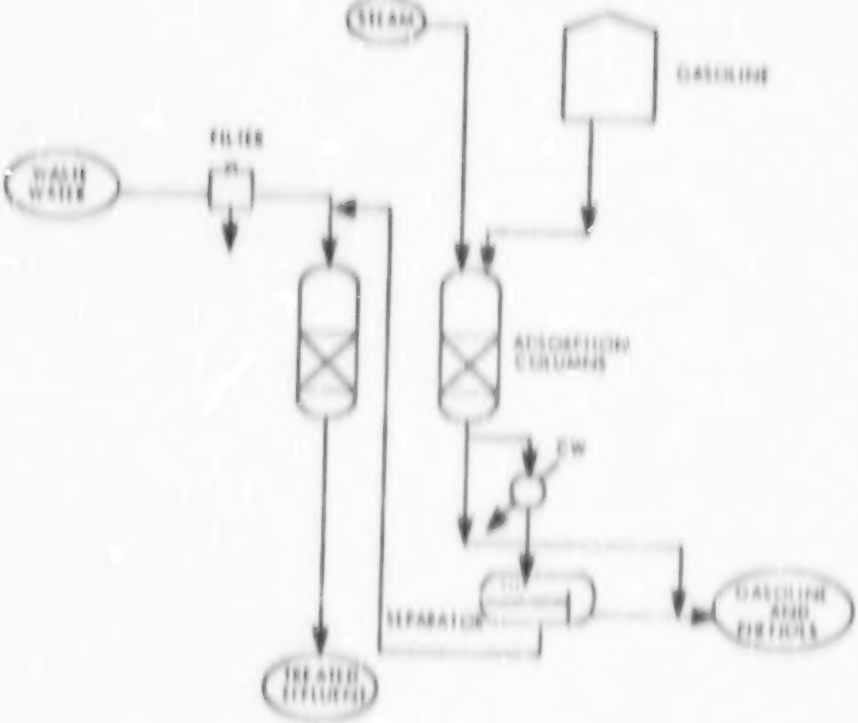

STEAM
GASOLINE
FILTER
WASH WATER
ADSORPTION COLUMNS
CW
SEPARATOR
GASOLINE AND PHENOLS
TREATED EFFLUENT

Figure 17-7. Phenol recovery by adsorption with gasoline regeneration.

TABLE 17-3 COSTS OF PHENOL RECOVERY BY VARIOUS METHODS

Basis: 10^6 lb water/hr with 6000 ppm phenol, 99% removal

Note: See text - different systems are not directly comparable

	Adsorption with acetone regeneration	Adsorption with gasoline regeneration	Liquid-liquid extraction with benzene
Capital Cost			
Adsorption and distillation systems.			
For adsorption resin, engineering, site preparation, development costs and license fee included	$ 9.3 × 10^6	$ 8.7 × 10^6	$9.22 × 10^6
Operating Cost	10^6 $/yr	10^6 $/yr	10^6 $/yr
Amortization and other capital related expenses at 17%/yr	1.58	1.48	1.57
Steam at $1.80/$10^6$ Btu	2.27	1.64	1.97
Electricity at 2¢/kw-hr	0.02	0.02	0.08
Resin (5-yr life)	0.4	0.4	0
License royalty (if phenol is sold)	0.25	0.25	neg.*
Solvent makeup (acetone $1/gal)	0.46	neg.*	neg.*
	4.98	3.79	3.62

---

* Negligible

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SECTION 18

BIOLOGICAL TREATMENT

18.1 INTRODUCTION

In biological treatment of wastewater, dissolved and colloidal organic matter is subjected to action by bacteria and other microorganisms which remove organic matter from water by converting it, partly to carbon dioxide and partly to a settleable organic sludge consisting mostly of dead and live microorganisms. Organic matter is commonly measured as biochemical oxygen demand (BOD), chemical oxygen demand (COD) and total organic carbon (TOC). The efficiency of biological treatment is measured by the decrease in these parameters. Biological treatment can also be used to convert ammonia to nitrate (called nitrification) and to convert nitrate to nitrogen (called denitrification).

In this section various biological treatment systems are examined in terms of their capabilities for treating foul condensate from coal conversion processes. Also discussed will be field experience, design procedures and their limitations, and research needed if existing information is inadequate. Since there is no existing full-scale facility in the United States, most of the evaluation has to be based on the experience of treating wastewaters with similar characteristics and on laboratory studies of coal conversion wastewaters. Under certain circumstances educated guesses were necessary; the assumptions made are clearly stated and can be tested and modified as more information becomes available.

A long history exists in the treatment of industrial wastes containing phenolic compounds, and these wastes are amenable to aerobic biological treatment.[1,2,27,30] Acceptable treatment may be achieved using trickling filters or activated sludge systems. Most of these studies are related to coke plant wastes, while a limited number of laboratory studies[3] on coal conversion wastes are available. However, it has also been noticed that appropriate safeguards must be provided against process upsets, and inorganic macro and micro nutrients may have to be added to ensure the success of aerobic biochemical oxidation.[3,4] In this case these include not only the common nutrient, phosphorous, but also various inorganic trace nutrients such as metals which are required by activated sludge but are not available in the wastewater.[4]

In the area of anaerobic biological treatment, little is known regarding its capability for treating phenolic wastes. A similar situation exists with the biological removal of nitrogenous oxygen demand and nutrients, which require a combination of nitrification and denitrification following an acceptable removal of carbonaceous oxygen demand.

In order to identify the optimal biological treatment system for coal conversion wastewaters, the following systems have been studied and a preliminary design provided for costing purposes where possible:

Air Activated Sludge (AAS) System
High Purity Oxygen Activated Sludge (HPOAS) System
Activated Trickling Filter--High Purity Oxygen Activated Sludge
(ATF-HPOAS) System
Air Activated Sludge--Nitrification-Denitrification (AASND) System
Anaerobic Treatment System

Each system has been studied for the exemplary wastewater shown on Table 18-1. Comparisons of the results in Section 18.3 through 18.6 show that the system consisting of an activated trickling filter followed by a high purity oxygen activated sludge process has the lowest cost, has good stability and controllability and reduces BOD to the lowest level. Furthermore, the design of the high purity oxygen activated sludge system was more conservative than the design of the air activated sludge system, which emphasizes the correctness of our choice. The activated trickling filter followed by a high purity oxygen activated sludge process is used for all cost estimating on the complete treatment plants discussed in Section 19. As shown on Table 18-16, cost estimates were made for this system using several BOD loadings and

TABLE 10-1. CHARACTERISTICS OF EXEMPLARY COAL CONVERSION WASTEWATER

Flow	1×10^7 gallons/day = 1.04×10^6 lb/hr
Phenol	6000 - 6600 mg/l as C_6H_5OH
BOD_5	≈ 18,000 mg/l
COD	26,000 - 30,000 mg/l
NH_3	≈ 3,500 mg/l as N
pH	5.5* to 7.0
Ca + Mg	< 100 mg/l
Na	≈ 100 mg/l
Cl	≈ 500 mg/l

*Approximate pH for 6,300 mg/l pure C_6H_5OH solution.

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throughputs. For the Hygas plants, which have the lowest BOD loading and low throughput, the cost has been estimated as $0.025/lb BOD removed. For all the other plants the cost has been estimated as $0.021/lb BOD removed. Each system requires 10.18 kw-hr + 1900 Btu as steam/lb BOD removed.

10.2 EQUALIZATION

A feed of nearly constant characteristics can eliminate the upsets due to shock loads or abrupt changes in composition and is essential for treating high-strength wastewaters by biological means. Recent batch studies[5,6] on coke and petroleum refining wastewater treatment by biological processes have reaffirmed this requirement.

In many respects the exemplary coal conversion wastewater described in the last subsection is very similar to the coke plant wastewaters, characterized by high concentrations of phenol, ammonia, BOD and COD. As a first approximation the field experience on the treatment of coke plant wastewaters has been used for coal conversion wastewaters. For coke plant wastewaters it has been recommended[7] that a storage capacity equal to five or more days of feed liquor be provided for equalization. In an existing activated sludge plant treating coke plant wastewater, the storage capacity of the equalization basin is on the order of 7.4 days.[8] A period of 7.4 days of storage has been used to calculate costs of the storage basins, which were assumed to be approximately square, 10 feet deep with concrete walls and base one foot thick. Cost is then estimated by taking the concrete at $100 per cubic yard.

18.3 AIR ACTIVATED SLUDGE (AAS) SYSTEM--SCALED PLANT

The air activated sludge (AAS) system is probably the most common treatment system used for wastewaters with constituents similar to coal conversion wastewaters, e.g., coke plant wastes. An extensive literature review on the biological oxidation of coke plant wastes was reported by Barker and Thompson[9] in 1973. Among the treatment systems discussed, AAS is the predominant treatment system of success. Laboratory studies[2] abroad have also indicated that AAS systems can satisfactorily treat the coal conversion wastes with the following characteristics:

total ammonia	~1,550 ppm
total phenols	~300 ppm
thiocyanate	~150 ppm
chloride	~2,500 ppm

Field Experience

Since much experience on the treatment of coke plant wastes will be utilized in the following discussion, it is appropriate to summarize on Table 18-2 the typical compositions[5] of coke plant wastes, compositions after ammonia distillation, and after both ammonia distillation and phenol extraction. In comparison with the exemplary coal conversion wastewater listed on Table 18-1 and the analytical data in Section 14-2, the coke plant waste (excess ammoniacal liquor) has a comparable ammonia content, larger concentrations of cyanide, thiocyanate and chloride, and less of phenol.

One of the most important considerations regarding biological treatment of coke plant wastes is to determine if the waste contains any inhibitory

TABLE 18-2. TYPICAL ANALYSIS OF AMMONIACAL LIQUOR AND STILL WASTE

	Excess Ammoniacal Liquor	Undephenolized Still Waste	Dephenolized Still Waste
	Concentration (ppm)	Concentration (ppm)	Concentration (ppm)
Ammonia	3800	155	110
Phenol	1500	1320	158
Cyanide	20	0	0
Thiocyanide	600	0	0
Sulfide	2	0	0
Chloride	7000	4350	5400

constituents which may render the biological treatment system totally or partially unfunctional. If these constituents exist it is essential to determine their threshold concentrations and thus the dilution required for the influent to the biological treatment system. Field experience with coke plant wastes at municipal sewage plants has shown that phenols may be successfully reduced to less than 1 mg/l if they are diluted by municipal sewage at a ratio of between 6 and 19 to 1, i.e., coke plant wastes constituting about 15 percent to 0.5 percent of the influent to biological treatment system.[9] Dilution may also be achieved by internal recirculation of treated water rather than the use of an external dilutant.

The constituents of inhibitory potential to the AAS system include phenol, ammonia, chloride and refractory organics in the coal conversion wastewaters. The threshold concentration of phenol has been reported at the level of 500 mg/l;[10] however, as phenol is readily utilized in the aeration tank of activated sludge systems, its concentration in a completely mixed aeration tank is not likely to exceed this level. The inhibitory effect of ammonia on the AAS system has been well recognized in several full-scale designs where ammonia concentration in the aeration unit is maintained at 1,200[9] to 2,000[8] mg/l or less. Although nitrogen is an essential nutrient for the growth of activated sludge, its consumption in the AAS system is far less than that of phenol and thus may dictate the dilution requirement. As for chloride, no detrimental effect to the AAS system is expected if the chloride concentration does not exceed 2,000 mg/l.[9]

The refractory organics, as commonly measured by the difference between COD and BOD, may also affect the performance of the AAS system and the dilution necessary for efficient treatment. Unfortunately this appears to be a most important, but poorly understood, parameter. Any definite information in this regard can only be obtained by pilot testing with the specific wastewater to be treated.

Design Criteria

Because of the inhibition of biological processes by ammonia and the need to remove ammonia, two alternative schemes have been considered:

(1) Ammonia recovery (probably by distillation) followed by AAS system.

(2) Dilution of ammonia followed by AAS system and further removal of ammonia in subsequent processes.

Ammonia distillation is discussed in Section 16, and the three-sludge system for ammonia removal is detailed in Section 18.5.

The design criteria for biological treatment of coke plant wastes are potentially useful for coal conversion wastewater treatment. Some typical design criteria are shown on Table 18-3. Based on the information of Table 18-3, the ability of the AAS system to remove phenols to a level of less than 1 mg/l appears to be consistent, while key design parameters like F/M ratio vary over a wide range. The most complete data are available under column (1), representing the design at Bethlehem Coke Plant, Bethlehem, Pennsylvania where a full-scale biological treatment facility has been in operation since 1962.

Scale-up From Coke Plant Wastewater Treatment

One approach to designing a treatment facility without pilot tests and adequate data base is to scale from an existing facility on the basis of key design parameters. The Bethlehem Coke Plant has successfully removed phenols and BOD for years, and rather complete design and operation data are

TABLE 18-3. TYPICAL DESIGN CRITERIA FOR BIOLOGICAL TREATMENT OF COKE PLANT WASTES

	(1)	(2)	(3)	(4)
Influent Dilution	Yes	*	Yes	*
NH_3 Concentration in aeration unit mg/l	2,000	*	<1,200	*
pH	6 - 8	7 - 8	*	*
Weight ratio of phenol to P	70	*	*	*
Temperature of aerated water, °F	80 - 95	>70	*	*
F/M, lbs phenol per lb MLSS per day	0.7	0.2 to 0.25	*	0.16 to 0.3
MLSS, mg/l	3,300-4,700	2,500-3,500	*	2,500-3,000
Aeration time, hrs	56[a]	24	37	116
Influent phenol concentration, mg/l	∿1,600	250-475	260-400	1,000
Effluent phenol concentration, mg/l	<0.1	0.1-0.3	0.8-3.6	0.1
BOD removal, %	85-95	*	*	*

---

* No data available

a. Based on undiluted wastewater flow

(1) Data from Reference 8

(2) Data from Reference 9, for Lone Star Steel Co., Texas

(3) Data from Reference 9, for Dominion Foundries & Steel of Hamilton, Ontario

(4) Data from Reference 3, for Alan Wood Steel Co., Pennsylvania

available in the literature.[8] As an introduction to activated sludge systems, such a scaled design has been made and costed. Theoretical design procedures are discussed in the next section.

As pointed out, two treatment schemes are possible for ammonia removal. In Scheme 1, ammonia is removed by distillation leaving just sufficient ammonia nitrogen in the influent to the biological system to meet the nutrient requirement. Scheme 2 will provide adequate dilution so that the ammonia concentration in the biological reactor will not exceed the inhibitory level of 2,000 mg/l, and certain further treatment of ammonia (e.g., nitrification and denitrification) will be necessary following the removal of carbonaceous BOD. The major difference between the two schemes lies in the hydraulic load to the clarifiers. Scheme 2 requires larger clarifiers because of the added dilution flow.

The scaled design is based on the assumption that the biodegradability of coal conversion wastewaters is identical with that of the coke wastewater. This assumption may well be open to question. No data on COD of the coke wastewater is given by Kostenbader and Flecksteiner.[8] However, an analysis of an average coke plant waste indicated that the theoretical oxygen demand due to phenols, which are readily biodegradable, constitute about 68 percent of the measured COD while for coal conversion wastewater phenol averaged about 40 percent of the COD.[11] Although the question of biodegradability can only be answered fully by pilot testing, the above comparison indicates certain differences in chemical composition between coke plant and coal conversion wastewaters. It is essentially unknown at this point whether and how this will affect the design of biological treatment. Should the assumption of biodegradability become invalid to any extent, there would be corresponding limitation on the usefulness of the preliminary design.

The following rules were used to produce the scaled design.

Nutrients such as N and P are essential for biological treatment. The required weight ratio is assumed to be invariant and is phenol:N:P = 70:5:1. Assuming an average phenol concentration of 6,300 mg/l (6,000-6,600 mg/l), the concentration of N and P required will be 450 mg/l and 90 mg/l respectively. Excess N is available in the wastewater, and for Scheme 1 the ammonia nitrogen concentration will be reduced to 450 mg/l by distillations prior to biological treatment. Phosphorus will have to be supplied by the addition of phosphoric acid or equivalent.

The phenol loading rate to the aeration tank is taken to be constant and has been determined to be 12 lb phenol/(day)(10^3 ft^3) or less, and 0.7 lb phenol/(day)(lb MLSS) or less.[8] For the actual scale-up the following are used: 11.1 lb phenol/(day)(10^3 ft^3) and 0.45 lb phenol/(day)(lb MLSS).

The aerator power requirement is taken to be proportional to the BOD or phenol removed. At Bethlehem Coke Plant the power requirement is based on 18.2 lb phenol removed/(day)(hp), or 43.3 lb BOD/(day)(hp)--calculated on the basis of 2.38 lb BOD per lb phenol--which compares closely with typical values in the literature of 45-50 lb BOD removed/(day)(hp).[12]

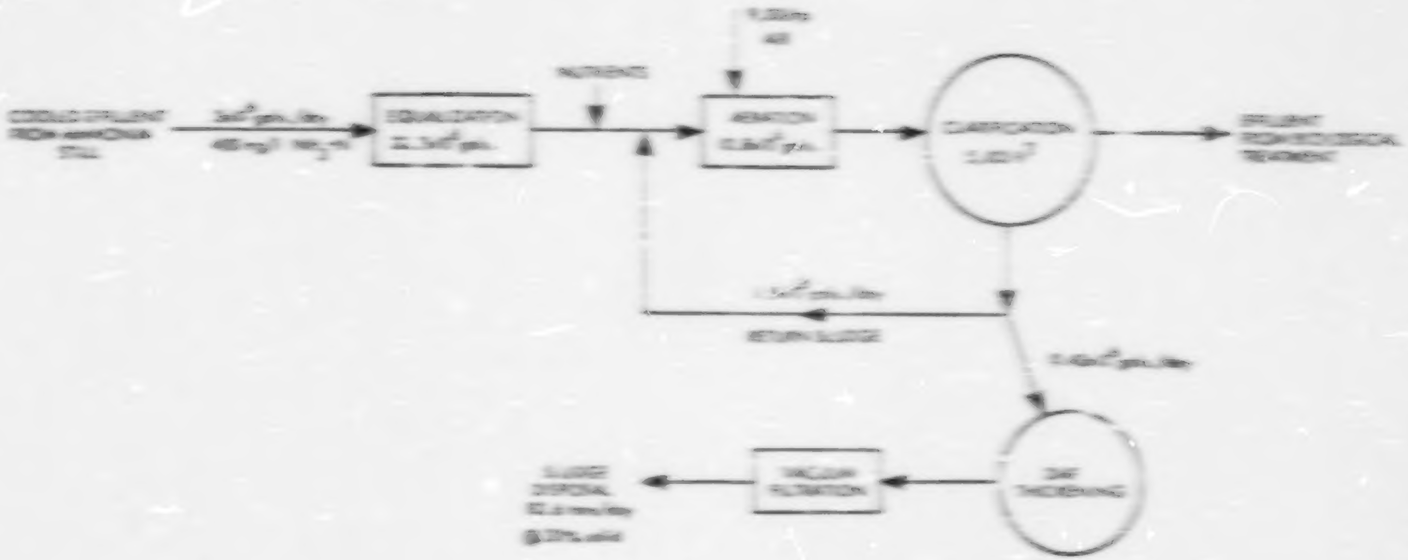
Sludge generation at Bethlehem Coke Plant is reported to be 0.2 lb sludge produced/lb phenol treated at a phenol loading rate of 1,300 lb/day and a waste sludge rate of 3,300 gal/day. The solids concentration in the clarifier underflow can thus be calculated to be about 9,500 ppm. When these numbers are used to scale, the required plant has a return sludge flow of about 1.5 × 10^6 gal/day and a waste sludge flow of 0.42 × 10^6 gal/day. The mean cell residence time in such an AAS system will be about 10-11 days. The quantity of sludge to be disposed of will be about 16.5 tons dry solids per day.

The surface area of clarifiers is determined on the basis of a hydraulic loading of about 685 gpd per square foot.

For the treatment of sludge, the following design criteria are used: 25 lbs dry solids per square foot per day for the dissolved air flotation (DAF) thickener, and 120 lbs dry solids per square foot per day for vacuum filters. These values are assumed,[28] not scaled, because Bethlehem Coke Plant discharges its sludge to a sewage plant and provides no sludge treatment.

The preliminary design of the AAS system for Schemes 1 and 2 is shown on Figures 18-1 and 18-2. Figure 18-3 shows the general configuration of aeration basins, used for costing purpose. The major difference in the design between Schemes 1 and 2 lies in the size of clarifiers because of different hydraulic loads.

The power requirement for aerators is estimated to be 9100 hp and is a



EFFLUENT FROM AMMONIA STILL
EQUALIZATION
NUTRIENTS
AIR
AERATION
CLARIFICATION
EFFLUENT FROM BIOLOGICAL TREATMENT
RETURN SLUDGE
DAF THICKENING
VACUUM FILTRATION
SLUDGE DISPOSAL

Figure 18-1. Air activated sludge system (Scheme 1).

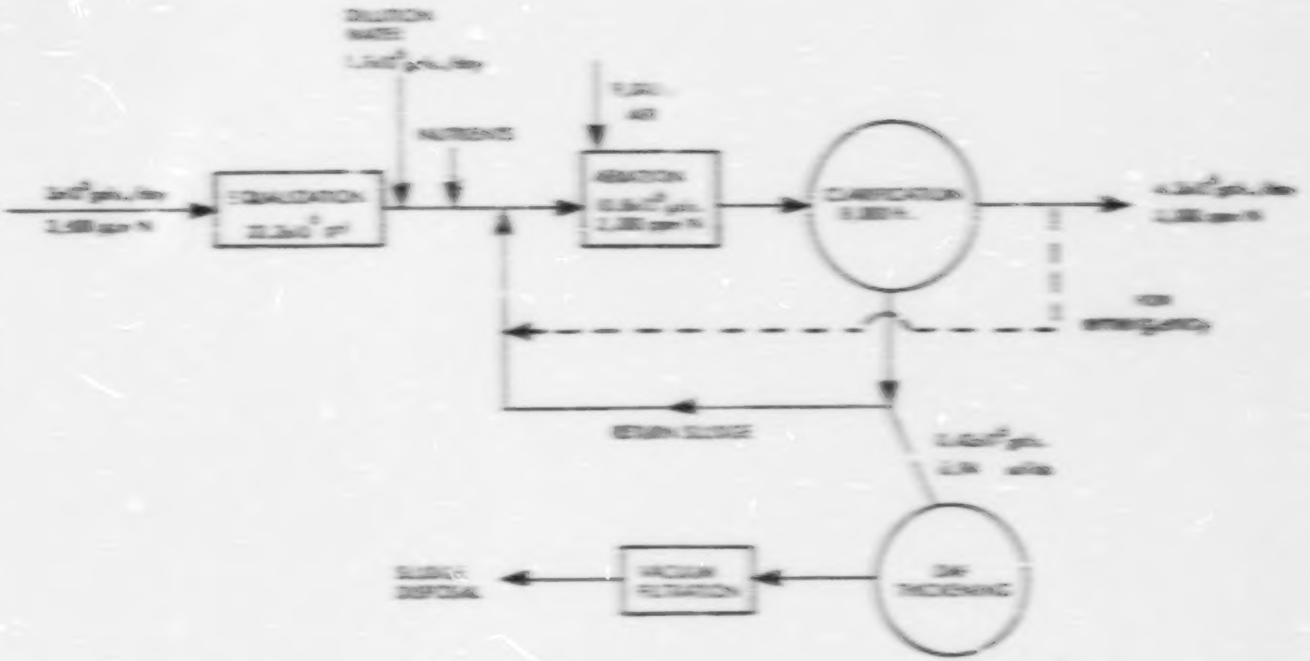

DILUTION
WATER
EQUALIZATION
NUTRIENTS
AIR
AERATION
CLARIFICATION
FOR
EMERGENCY
RETURN SLUDGE
DAF
THICKENING
VACUUM
FILTRATION
SLUDGE
DISPOSAL

Figure 18-2. Air activated sludge system (Scheme 2).

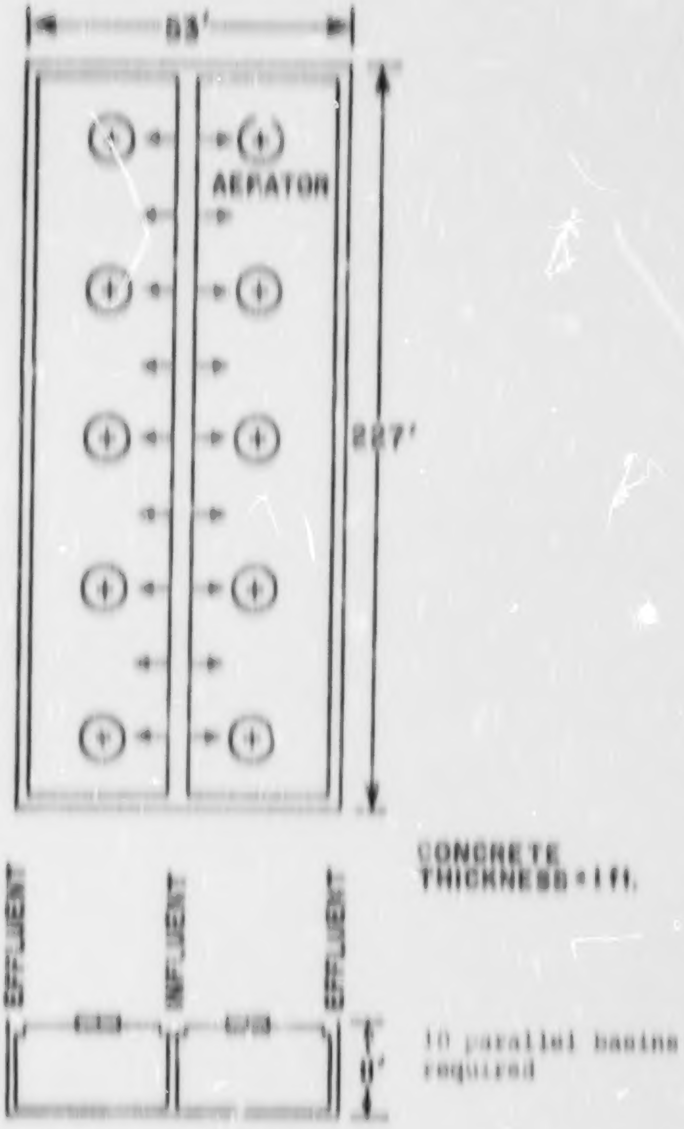

53'
AERATOR
227'
CONCRETE THICKNESS=1ft.
EFFLUENT
INFLUENT
EFFLUENT
8'
10 parallel basins required

Figure 18-3. Typical configuration of an aeration basin for air activated sludge systems.

highly significant outlay of capital and operating costs. Since this power requirement is directly related to the BOD removed and has essentially nothing to do with the ammonia concentration, no difference in power requirement is expected between Schemes 1 and 2.

According to the Bethlehem Coke Plant experience, about 0.1 mg/l phenol or less is found in the effluent when the influent contains about 1,400 mg/l phenol.[8] Now that the influent contains about 6,800 mg/l phenol, phenol in the effluent may be about 0.5 mg/l. The reported BOD removal at Bethlehem Coke is about 85-95 percent, so 10 percent of the influent BOD of about 18,000 mg/l may remain in the effluent, i.e., 1,800 mg/l. No COD data is available at Bethlehem Coke Plant, but the COD removed will not be less than the BOD removed. So the COD may be expected to be reduced from about 28,000 mg/l to 11,800 mg/l. In summary, the effluent characteristics of the AAS system may be as follows:

Phenol	~0.5 mg/l
BOD	~1,800 mg/l
COD	~11,800 mg/l

Cost of Scaled Plant

The costs of the AAS systems, calculated according to Table 18-4, are shown on Tables 18-5 and 18-6. The difference in costs between Schemes 1 and 2 appears to be negligible, and the total cost of treatment is about $3.2/1,000 gallons.

18.4 THEORETICAL DESIGN OF AIR ACTIVATED SLUDGE SYSTEMS

The performance of an activated sludge process depends on biochemical transformation and subsequent solid-liquid separation. In principle, a rational design would have to be based upon the mechanism of these processes. The mechanism in the activated sludge process is generally represented by kinetic models which invariably involve the application of certain fundamental coefficients. Two such models for biochemical transformation, the Monod model and the first order approximation, have recently been utilized for the

TABLE 18-4. COST ESTIMATION PROCEDURE FOR AIR ACTIVATED SLUDGE PLANT

Capital Costs		
Aeration Basin:	See Figure 18-3 Cost based on volume of concrete at $240/yd^3	
Aerators		$600/installed hp
Clarifiers		Figure 15-3
Cooling Towers		$10/gpm circulated
Dissolved Air Flotation Thickeners		Figure 18-4
Rotary Vacuum Filters		Figure 18-4
Operating Costs		
Amortization and other capital related items		15% of capital/yr
Maintenance:	Concrete	1% of capital/yr
	Machinery	2% of capital/yr
Electricity		2¢/kw-hr, 8,000 hrs/yr
Phosphorus		42¢/lb P

design of activated sludge process.[13] The first order approximation has been found valid if the influent BOD does not exceed 500 mg/l and the effluent soluble BOD is less than about 90 mg/l.[14] It is therefore considered not applicable in the treatment of these exemplary wastewaters which have an influent BOD far in excess of 500 mg/l. In the following paragraphs the Monod model will be used to estimate the size of aeration basins and the range of size variation by assuming reasonable values for fundamental coefficients.

Monod Model Calculations

In a completely mixed activated sludge system, the mean cell residence time θ_c, hrs, may be related to the specific growth rate of the microorganism μ, hrs^{-1}, and the microorganism decay coefficient b, hrs^{-1}, by

$$\frac{1}{\theta_c} = \mu - b \qquad (1)$$

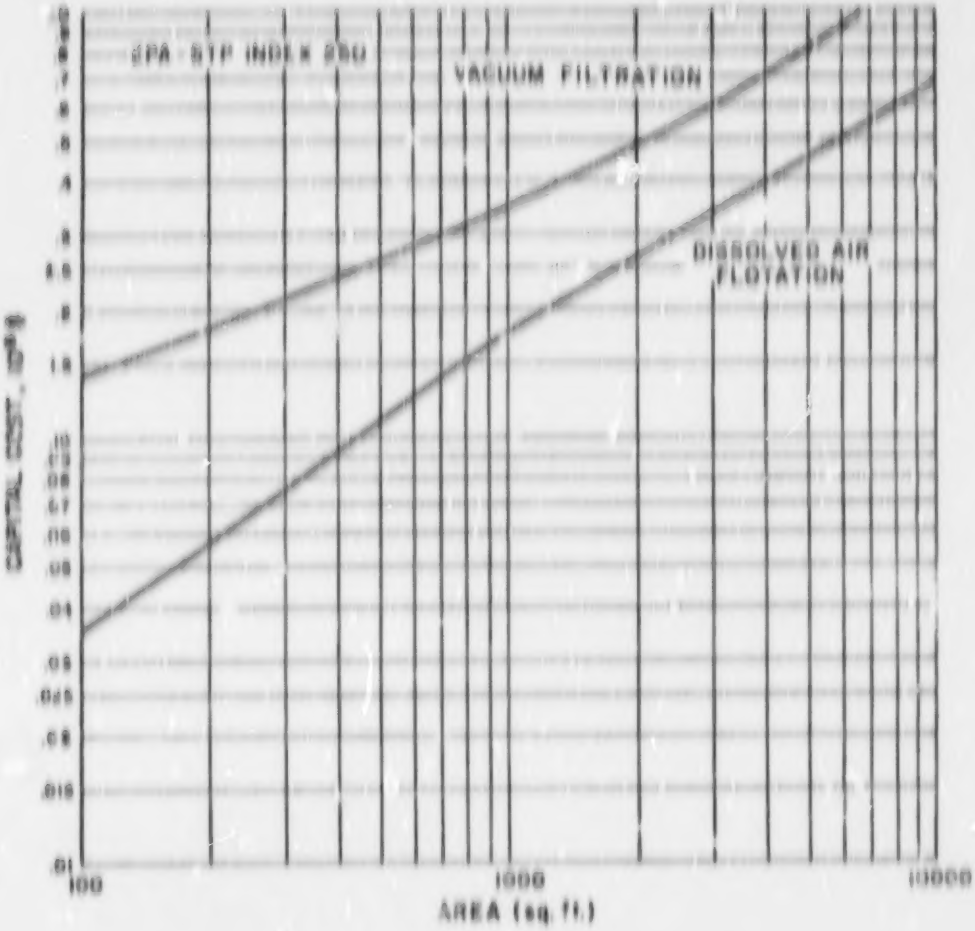


Figure 15-4. Capital cost of vacuum filtration and dissolved air flotation (from Reference 12).

TABLE 18-5. COSTS OF AIR ACTIVATED SLUDGE SYSTEM (SCHEME 1)

Capital Costs	10^6 $
Equalization	1.19
Aeration Basin	2.18
Aerator	5.60
Clarification	0.23
DAF Thickening	0.54
Vacuum Filtration	0.36
TOTAL	10.10

Operating Costs	10^6 $/yr
Amortization & other capital-related items @ 15% of capital/yr	1.52
Maintenance	
of Concrete work	0.04
of Machinery	0.12
Electricity @ 7500 kw	1.20
Chemicals:	
Phosphorous	0.32
TOTAL	3.20

TOTAL ANNUAL COST = 3.2 × 10^6 $/y
= 3.2 $/1,000 gallons

TABLE 18-6. COSTS OF AIR ACTIVATED SLUDGE SYSTEM (SCHEME 7)

Capital Costs	10^6 $
Equalization	1.19
Aeration Basin	2.38
Aerator	5.60
Clarification	0.29
DAF Thickening	0.54
Vacuum Filtration	0.36
TOTAL	10.16
Operating Costs	
Amortization & other capital-related items @ 15% of capital/yr	1.52
Maintenance	
Concrete work	0.06
Machinery	0.12
Electricity @ 7500 kw	1.20*
Chemicals	
Phosphorous	0.32
TOTAL OPERATING COSTS	3.20

TOTAL ANNUAL COST = 3.2 x 10^6 $/yr
= 3.2 $/1,000 gallons.

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*Including requirements for aeration and pumping of dilution water

The Monod model then relates μ to the soluble substrate concentration S which may be expressed in terms of BOD or equivalent

$$\mu = \frac{\mu_m S}{K_s + S} \tag{2}$$

where

μ_m = maximum specific growth rate of the microorganisms (hrs^{-1})
K_s = saturation constant; i.e., the substrate concentration when μ is one-half of μ_m

According to equations (1) and (2), Θ_c may be determined by assuming proper values for S, K_s, μ_m and b. Furthermore, the volume of aeration basins can be determined from Θ_c and the following parameters:

S_0 = influent soluble substrate concentration (mg/l)
Y_g = true growth yield (mg MLSS)/(mg BOD removed)
X = microorganism concentration in aeration basin (mg/l)
Q = influent flow rate to aeration basin (gal/hr)

using the equation[13]

$$X\Theta = \frac{Y_g(S_0 - S)}{(1/\Theta_c) + b} \tag{3}$$

where Θ is the hydraulic residence time and equals (volume of aeration basin)/Q.

However, in the determination of Θ_c some practical constraints have to be observed. Experience shows that Θ_c should be kept in the range of 3 to 14 days to achieve an activated sludge that flocculates well.[13]

Assumptions

In our evaluation using the Monod model, attention has been primarily focused upon the BOD due to phenol, the most significant organic contaminant in the influent to the activated sludge process. Based on a phenol concentration of 6,600 mg/l, the S_0 in terms of BOD is assumed to be 2.38 × 6,600 = 15,700 mg BOD/l. The microorganism concentration in aeration basins, X, is assumed to be equal to the MLSS (mixed liquor suspended solids) because the influent concentration of suspended solids is considered insignificant and X is assumed to be equal to 4,000 mg/l. The influent flow rate is 3×10^6 gpd, or 2,083 gpm.

The other parameters necessary for our evaluation are S, b, μ_m, K_s and Y_g. The value of S depends on the BOD removal percentage and the following values have been used:

Case	A	B	C	D
% phenol removed	99.99	99.98	99.97	99.0
S, mg/l BOD	1.2	2.4	5	160

For the fundamental coefficients, b, μ_m, K_s and Y_g, four sets of values have been selected and are shown on Table 18-7.

TABLE 18-7. VALUES OF FUNDAMENTAL COEFFICIENTS USED IN THE MCKOD MODEL EVALUATION

Coefficients	b $(hr)^{-1}$	μ_m $(hr)^{-1}$	K_s mg/l BOD	Y_g mg MLSS produced per mg BOD removed
Set 1*	0.0025	0.55	120	0.5
Set 2	0.0025	1.65	120	0.5
Set 3	0.0025	0.55	120	0.084***
Set 4	0.0104**	1.65	120	0.084

---

*Typical values for domestic sewage.[13]

**Typical value for refinery wastewater.[13]

***Typical value for coke plant wastewater.[8]

The values of the coefficients in Set 1 are those typical of domestic sewage and are used as the basis for modifications in the other sets. The oxidation of phenol appears to be more efficient than the BOD removal from domestic sewage. At Bethlehem Coke Plant[8] more than 99 percent of phenol was removed at a phenol loading of 0.7 lbs phenol per day per lb MLSS, or an equivalent BOD loading of about 1.7 lbs BOD per day per lb MLSS, which is much higher than those used for domestic sewage, namely, 0.2 to 0.6 lbs BOD per day per lb MLVSS.[15] For both applications θ_c is in the range 5 to 15 days, and the MLSS in the range 3,000 to 6,000 mg/l. This indicates that in comparison with domestic sewage the coefficients for phenol-bearing wastes may include a larger μ_m or smaller Y_g, or both. This reasoning is reflected in our modification of the coefficients in Sets 2 through 4. In Set 4 we also tried a value of b which is typical of refinery wastewater.

Using the values of the fundamental coefficients and S, the volume of aeration basins was determined in accordance with the Monod model and the results are summarized on Table 18-8.

TABLE 18-8. VOLUME OF AERATION BASIN BASED ON MONOD MODEL

Set of Coefficients	Volume of Aeration Basin,† 10^6 gals				
	Case:††	A	B	C	D
1		45	21	*	*
2		15	*	*	*
3		8	4	*	*
4		27	*	*	*

---

† MLSS = 4,000 mg/l, S_0 = 15,700 mg/l BOD.

†† Based on concentration of S.

*Unsatisfactory as θ_c < 3 days.

When compared to the volume calculated by scaling the AAS system, namely, 10.85 million gallons, the values on Table 18-8 show a variation from about one half to four times. It is interesting to note that in most cases the criterion of a θ_c larger than three days cannot be met and, presumably, under those conditions poor flocculation of microorganisms would result and the effluent quality would tend to deteriorate as the suspended solids concentration increases. Alternatively one can say that in these cases the size of the aeration basin is controlled by θ_c and not by the removal rate of BOD.

In conclusion it does not seem feasible to size the aeration basin on the basis of inadequately known fundamental coefficients. The use of limited information on coke plant wastes as the only basis for comparison is also not completely satisfactory. In future pilot studies it is highly recommended that these fundamental coefficients be evaluated so that a rational design based on their values and the mathematical models presently available can be made possible.

18.5 AIR ACTIVATED SLUDGE--NITRIFICATION-DENITRIFICATION (AASND) SYSTEM

Scheme 2 of the AAS system requires further treatment to remove ammonia. Ammonia stripping is ruled out because of the air pollution and odor problem. One possible alternative is to remove ammonia biologically through nitrification and denitrification. An extensive description of these processes has been given by Barber and Thompson.[9]

Field Experience

Most of the field experience available to date comes from municipal wastewater treatment. An extensive collection of design criteria and procedures is available in the literature.[16] The use of an AASND system for removing carbon and nitrogen compounds from coke plant wastes is limited to pilot plant scale.[9] The information obtained from these two sources has been used as the primary basis of the preliminary design and subsequent cost estimate.

A continuous-flow pilot plant study to evaluate the feasibility treating coke plant wastes by the AASND system was reported in 1973. The results of the study indicate that the AASND system can be used to remove organic carbon compounds and ammonia from diluted coke plant wastes. The overall treatment efficiencies obtained include removal of greater than 99.9 percent phenols, 80 percent COD and 90 percent ammonia. The level of ammonia removal depends strongly on the efficiency of ammonia oxidation to form nitrate in the nitrification stage as any subsequent conversion of nitrate to nitrogen is limited by the amount of nitrate available. However, the nitrifying organism has been found sensitive to many constituents in the coke plant wastes. Dilution and efficient operation of the carbonaceous unit are necessary to prevent inhibition and loss of nitrification efficiency. For instance, the ammonia removal percentage was found to decrease from 60 percent to 45 percent as the influent ammonia nitrogen concentration increased from 400 to 1,200 mg/l,[9] and ammonia-free water may be necessary for dilution. The BOD concentration in the influent to the nitrification unit, which depends on how well the carbonaceous unit operates, can significantly affect the nitrification efficiency. Unfortunately, this information on BOD is not available in this pilot study,[9] and it might at least partly account for the fluctuation in nitrification efficiency.

Design

The design criteria developed from municipal experience and summarized in an EPA technology transfer publication[16] has been used for the preliminary design. Additional information gained from the pilot study on coke plant wastes[9] has also been utilized. This includes the limiting ammonia nitrogen concentration in the influent to the nitrification unit based on a certain level of treatment efficiency. Concentrations of the various nitrogenous species in the transformation process are summarized on Table 18-9. The carbon removal unit has already been designed in Section 18-3. In nitrification and denitrification, the reaction is the same regardless of the waste medium, whether it is municipal sewage, coke plant wastes or coal conversion wastes. However, the waste constituents besides ammonia may differ in their effects on nitrification and denitrification. In this preliminary design

TABLE 10-9. CONCENTRATIONS OF NITROGENOUS SPECIES IN NITRIFICATION AND DENITRIFICATION PROCESSES

	mg/l		
	NH_4^+-N	NO_3^--N	Total N
Influent to Nitrification*	400	--	400
Influent to Denitrification	160	240**	400
Effluent from Denitrification	160	24***	184

---

*Dilution is required to reduce NH_4-N concentration from 2,000 to 400 mg/l.

**Assume 60% of NH_4^+-N is oxidized in the nitrification unit.

***Assume 90% of NO_3^--N is reduced in the denitrification unit.

these differences are assumed negligible, and the experience with municipal sewage and coke plant wastes is assumed transferable to coal conversion wastes.

The preliminary design of the AASND system is shown in Figure 10-5. For the nitrification process, 15.8 × 10^6 gallons/day of ammonia-free dilution water is necessary to reduce the influent ammonia nitrogen concentration to 400 mg/l; 86.9 tons/day of CaO and 39.1 tons/day of Na_2CO_3 are needed for pH control and provision of inorganic carbon respectively; and 4,035 hp are necessary to pump air into the water for the nitrification reaction. In the denitrification process, in addition to the reactors and clarifiers, 201 hp are needed for mixing, 40 hp for nitrogen gas release and 70.4 tons/day methanol for the provision of organic carbon. The treatment of sludge is essentially the same as that for the AAS system.

Costs

The costs of the AASND system calculated according to Table 10-4 are shown on Table 10-10. According to this cost estimate, the total cost is

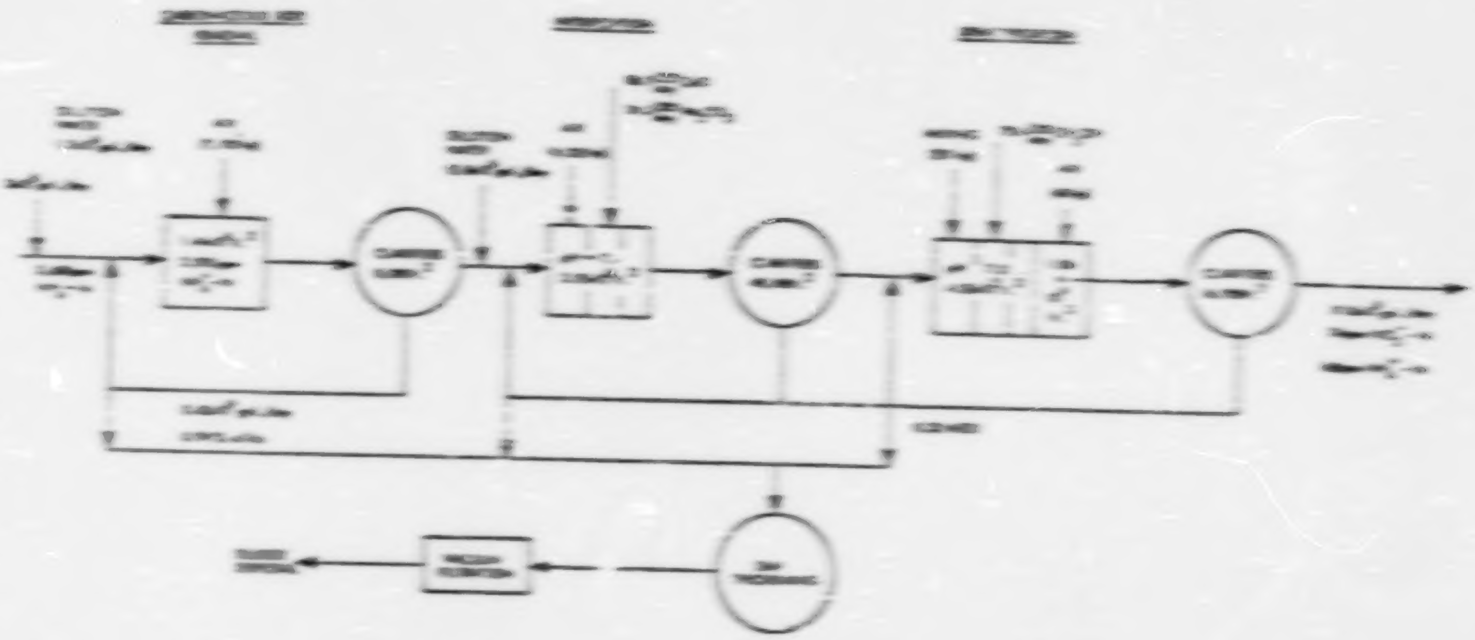

Figure 10-5. Air activated sludge—nitrification—denitrification system.

TABLE 18-10. COSTS OF AIR ACTIVATED SLUDGE-- NITRIFICATION-DENITRIFICATION SYSTEM

Capital Costs	10^6 $	
Equalization		1.19
Carbonaceous BOD removal		
Aeration Basins	2.38	
Aerators	5.40	
Clarification	0.29	8.07
Nitrification		
Aeration Basins	2.44	
Aerators	2.43	
Clarification	1.04	5.91
Denitrification		
Reactors	0.46	
Mixers & Aerators	0.14	
Clarification	0.51	1.11
DAF Thickening		0.60
Vacuum Filtration		0.68
TOTAL		17.56

Operating Costs	10^6 $/yr	
Amortization & other capital related items @ 15% of capital/yr		2.63
Maintenance		
Concrete Work		0.06
Machinery		0.17
Electricity		
Carbonaceous BOD @ 7,500 kw		
Nitrification @ 3,400 kw		
Denitrification @ 200 kw		
11,100 kw		1.78
Chemicals		
CaO 89.9 tons/day @ $54/ton	1.62	
Na_2CO_3 39.1 tons/day @ 70/ton	1.05	
CH_3OH 70.4 tons/day @ 127/ton	2.98	
P 1.1 tons/day @ 840/ton	0.32	5.97
TOTAL		10.61

TOTAL ANNUAL COST 10.61 x 10^6 $/yr = 10.61 $/1,000 gallons about $10.29/1,000 gallons, with the cost of chemicals constituting more than 50 percent of the total cost. Ammonia separation, with recovery of ammonia for sale as described in Section 16, is clearly the preferred procedure.

18.6 HIGH PURITY OXYGEN ACTIVATED SLUDGE (HPOAS) SYSTEM

The use of high purity oxygen, rather than air, as the source of oxygen for biological waste treatment has gained increasing acceptance in the water pollution control field. Because oxygen is required in many coal conversion plants, it can be made available for water treatment at the cheapest possible price. Approximately 3,000 tons/day of oxygen will be needed in a standard size SNG plant, and the amount of oxygen required for the HPOAS system may be about 10 percent of that required for coal conversion.

The use of an HPOAS system may have the following advantages over an AAS system:

(1) Smaller oxygenation basins, and thus lower space requirements

(2) Less susceptible to upsets due to shock loads, and thus more stable

(3) Less power required for mixing because of smaller oxygenation basins

(4) Less energy and cost for oxygen transfer, particularly when a large quantity of oxygen is produced on site

(5) Less water loss due to evaporation as the oxygenation basins are closed reactors.

To evaluate the HPOAS system, suppliers of these systems have been consulted, particularly Linde Division of Union Carbide Corporation. Their experience in the use of the HPOAS system for the treatment of coke plant waste, and in the pilot studies of HPOAS for treating coal gasification wastes, has been used to establish the criteria for a preliminary design.

Design

The HPOAS system design consists of multitrains in parallel, with each train consisting of multistages to obtain a quasi-plug flow condition. High purity oxygen is fed to the space above the liquor level in each stage of the oxygenation basin, and oxygen transfer is accomplished by use of surface aerators or equivalent. The dissolved oxygen concentration in the mixed liquor will be maintained at about 5 mg/l, rather than 2 to 3 mg/l as commonly used in the AAS system.

Because of the high strength of coal conversion wastes, a high level of treatment will be required. In order to reduce BOD to an acceptable level, taken to be less than 60 mg/l, two steps of HPOAS treatment are used with each step achieving about 95 percent removal of BOD.

Two key parameters for the design of activated sludge system are mean F/M (food to microorganism) ratio and MLVSS (mixed liquor volatile suspended solids). The F/M ratios for Step 1 and Step 2 differ because of the difference in BOD loading; F/M is 0.6 in Step 1 and 0.3 in Step 2. The MLVSS will be substantially larger than that for the AAS system because of improved settling velocities of the oxygen sludge, and the MLVSS in this case is assumed to be 7,300 mg/l in Step 1 and 4,500 mg/l in Step 2. The clarifiers are designed on the basis of an overflow rate of 400 gals/(day)(ft^2) in Step 1 and 300 gals/(day)(ft^2) in Step 2. The depth of the clarifiers is assumed to be 15 feet. The design is summarized on Table 10-11.

The oxygen requirement, pounds of oxygen required per pound of BOD removed, is a function of F/M and COD/BOD ratios.[17] The effect of COD/BOD ratio may be particularly significant in this case as the fate of COD in the biological treatment of coal conversion wastes is unknown at present. The oxygen requirement is assumed to be 1.03 lb/lb BOD removed in Step 1 and 1.21 lb/lb BOD removed in Step 2. Whenever COD needs to be evaluated in the biological treatment, the removal of COD is assumed to be equal to that of BOD; this assumption is conservative and should lead to a design on the safe side.

The average oxygen utilization in the oxygenation basin depends on the purity of the oxygen in the gaseous mixture which essentially consists of feed oxygen and the carbon dioxide produced as a result of the biochemical oxidation. Therefore the average oxygen utilization percentage will increase as the feed BOD concentration decreases and is assumed to be 75 percent in Step 1 and 80 percent in Step 2. Based on the oxygen requirement and average oxygen utilization efficiency, the amount of oxygen to be transferred can be

TABLE 10-11. DESIGN OF THE UNOX SYSTEM[a]

Design Basis	
Flow, 10^6 gal/day	3
BOD_5, lbs/day	450,000
BOD_5, mg/l	18,000
COD, mg/l	28,000
COD/BOD_5	1.56
Wastewater Temperature, °F	80°F
pH	Adjusted as required
Nutrients	Phosphorous to be added

System Design	Step 1	Step 2
Flow, Q(10^6 gal/day)	3	3
Retention Time, hrs (based on feed flow)	74	16
MLSS, mg/l	7,800	5,100
MLVSS, mg/l	7,300	4,500
Sludge Recycle Rate, %Q	35	75
Mean Biomass Loading, lbs BOD_5/(lb MLVSS)(day)	0.8	0.3
Volumetric Organic Loading, lbs $BOD_5/(10^3 ft^3)$(day)	364	84
Average D.O. level, mg/l	5.0	5.0
Oxygen Supplied, tons/day	278.9	16.1
Average Oxygen Utilization Efficiency, %	79	80
Secondary Clarifier Overflow Rate gal/(day)(ft^2)	400	300
Recycle Suspended Solids Concentration, wt %	2.0	2.0
Effluent Soluble BOD_5[b], mg/l	900	45

Utility Requirements	Oxygenation Motors		
	Step 1	Step 2	Total
Operating Energy:			
Brake HP	2,667	161	2,828
KW[c]	2,162	133	2,295
Connected Load:			
Nameplate HP	3,150	180	3,330

Maximum Single Connected Load = 100 hp, across-the-line, starting calculated.

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[a] Preliminary information supplied by Union Carbide on the basis of assumptions provided by WPA.

[b] Used as basis for determining oxygen requirement.

[c] Includes motor losses.

The energy requirement is estimated as follows. The surface aerators consume 1 hp-hr for 7.8 lb oxygen supplied, or 191 kw-hr/ton oxygen supplied. Air separation consumes about 330 kw-hrs/ton oxygen (Reference 89). Of this 330 kw-hrs, about 240 kw-hrs is required to drive the air compressors in the air separation plant. In coal conversion plants it is assumed that the air compressors are driven by steam turbines at 11,700 Btu/kw-hr, not by electricity. This leads to an energy requirement of 2.9×10^6 Btu as steam, plus 273 kw-hr per ton of oxygen. For quick estimating, as is necessary when doing the complete water treatment plant block diagrams in Section 19, a relationship is needed between the energy requirement and the BOD removed, not between the oxygen supplied and the BOD removed. An average figure of 1.31 lb oxygen produced/lb BOD removed and an energy requirement of 1,900 Btu as steam plus 0.018 kw-hr per lb BOD removed have been used.

A major design consideration is the control of water temperature in the oxygenation basin. It has been recommended[5] that the water temperature in the aerobic biological treatment of coke plant wastes be 95-100°F throughout the year. Attention must be paid to the temperature rise as a result of the biochemical oxidation reactions: the oxidation of about 165 mg BOD/l as phenol can theoretically cause 1°F temperature rise at these concentrations. Considering the various heat losses in oxygenation basins, it is assumed that the removal of 200 mg/l BOD will cause an increase in water temperature of 1°F. Since the removal of BOD in step 1 is 95 percent of 18,000 mg/l, this will result in a temperature rise of about 85°F. To maintain the proper temperature in the oxygenation basin, it will be necessary to recycle 12×10^6 gallons/day of the mixed liquor at a temperature of about 97°F and to reduce its temperature to 80°F in a cooling tower, as shown in Figure 18-6. This arrangement will also strip the CO_2 produced from the mixed liquor. The temperature of the 3×10^6 gallons/day feed is assumed maintained at 80°F from the equalization basin.

The preliminary design of the HPOAS system includes sizing the oxygenation basins and clarifiers, and determination of oxygen and electric power requirements. The procedures are outlined in the following paragraphs.

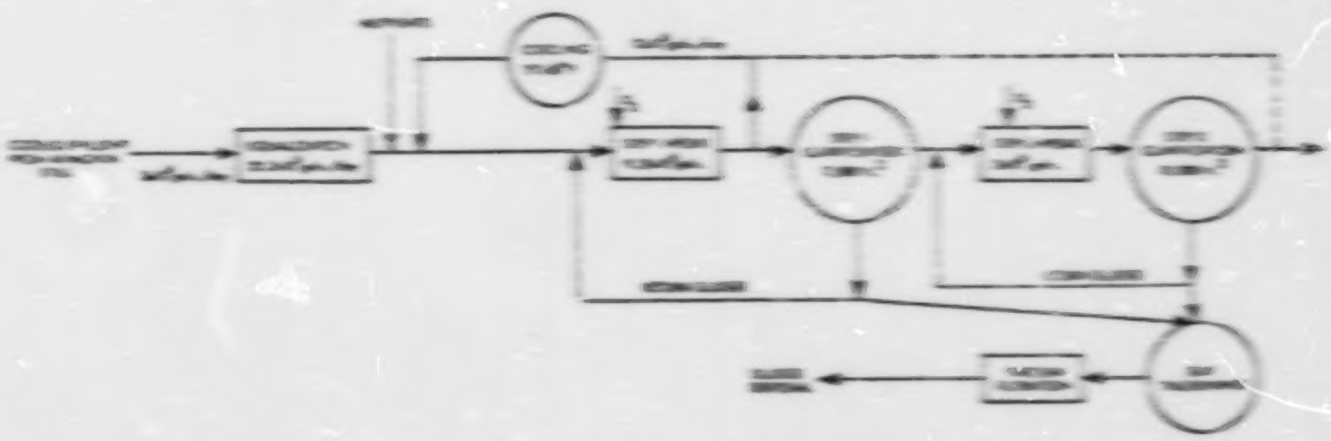


Figure 10-4. High purity oxygen activated sludge (HPOAS) system.

Oxygenation Basins

(1) Determine BOD (mg/l) to be removed on the basis of removal efficiency expected.

(2) Determine F/M and MLVSS (mg/l) from field experience or pilot studies.

(3) Calculate hydraulic retention time (RT_Q) by using the following equation:

$$RT_Q \text{ (hrs)} = \frac{\text{BOD (mg/l)} \times 24 \text{ (hrs/day)}}{\text{MLVSS (mg/l)} \times \text{F/M [lb BOD/(lb MLVSS)(day)]}}$$

(4) Calculate the total volume of the oxygenation basins (V) which is the product of RT_Q and Q (hydraulic feed rate).

(5) Calculate the total surface area (A) by assuming an economic water depth in the oxygenation basin, usually 15 feet, A = V/15.

(6) Determine the total number of stages to provide the area, each stage being a square in cross section.

(7) Design the overall configuration such that there are at least two parallel trains with at least three stages of the oxygenation basin in each train.

Recirculation of Mixed Liquor in Step 1

(1) Calculate the BOD removed in mg/l in Step 1.

(2) Calculate the temperature rise of mixed liquor on the basis of 1°F temperature rise per 200 mg/l BOD removed.

(3) Calculate the recycle flow required to hold the overall temperature rise in the mixed liquor passing through the oxygenation basin to about 15°F, from 80°F to 95°F. Assume that the cooling tower will lower the temperature of the recycled mixed liquor from 95°F to 80°F.

Clarifiers

(1) Assume the overflow rates for Steps 1 and 2 to be 400 and 300 gpd/sq ft respectively.

(2) Calculate the total surface area by dividing the hydraulic flow rate to the clarifiers with the overflow rate.

(3) Determine the diameter of clarifiers by considering the number of

clarifiers to be at least two and the diameter of each to be in the range of 30 to 100 feet.

(4) Assume the depth of clarifiers to be 15 feet for costing purposes.

Oxygen and Electric Power Requirement

(1) Calculate BOD removed in each step in pounds of BOD per day.

(2) Determine the oxygen requirement in terms of pounds of oxygen required per pound of BOD removed.

(3) Determine average oxygen utilization efficiency for each step according to the feed BOD concentration.

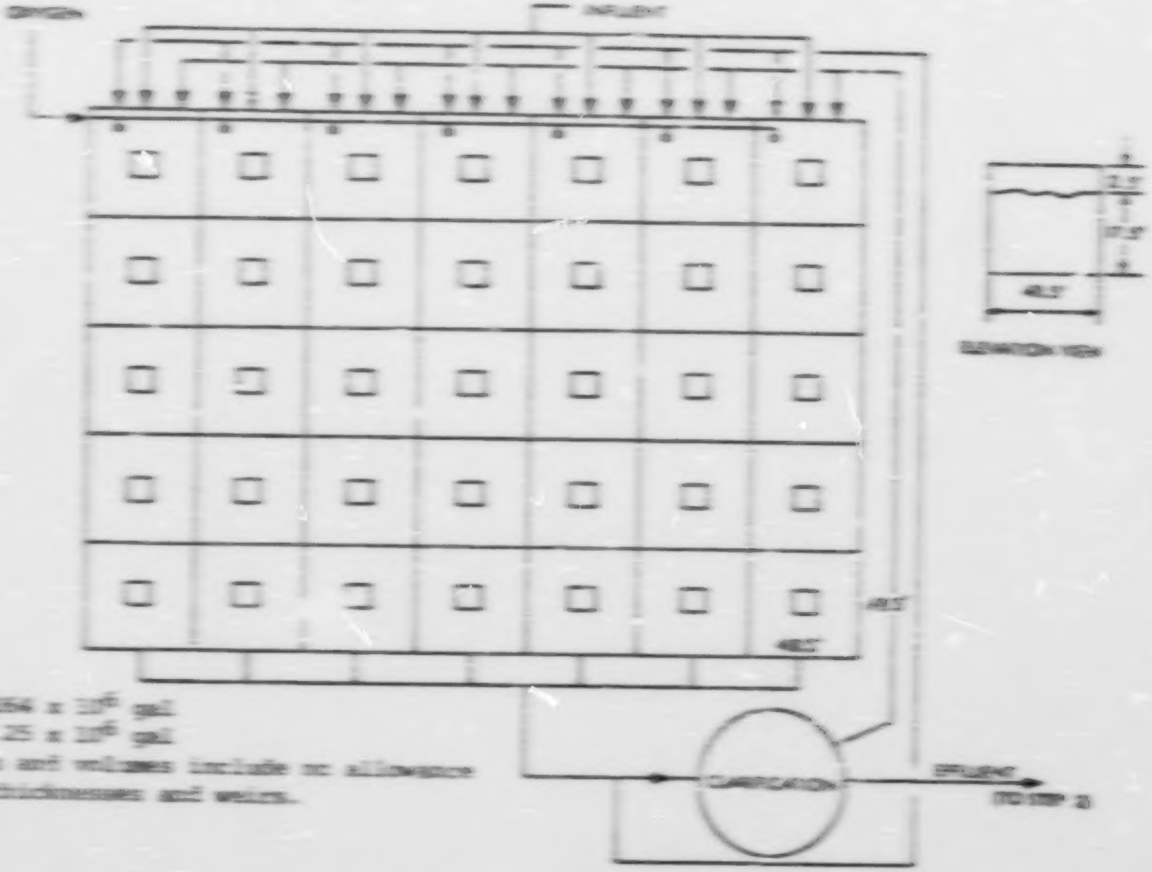
(4) Calculate the amount of oxygen to be transferred in pounds of oxygen per day.

(5) The energy required for oxygen transfer is about 191 kw-hr per ton of oxygen transferred, and that for oxygen generation is about 330 kw-hr per ton of oxygen generated (partly as drive steam and partly as electricity).

The flow diagram of the HPOAS system is shown in Figure 18-6. The design basis, system design and utility requirements are detailed on Table 18-11, which is preliminary information supplied by Union Carbide on the basis of assumptions provided by us. Step 1 consists of seven trains, each with five stages of concrete oxygenation reactors, while Step 2 consists of two trains each with three stages. Their detailed configurations are shown in Figures 18-7 and 18-8. It should be pointed out that 12 × 10^6 gal/day of the mixed liquor from Step 1 will be recycled through a cooling tower to reduce the water temperature from 95° to 80°F and to strip off CO_2. The broken line in Figure 18-6 shows the recycling of the clarified water through the cooling tower for more flexible operation.

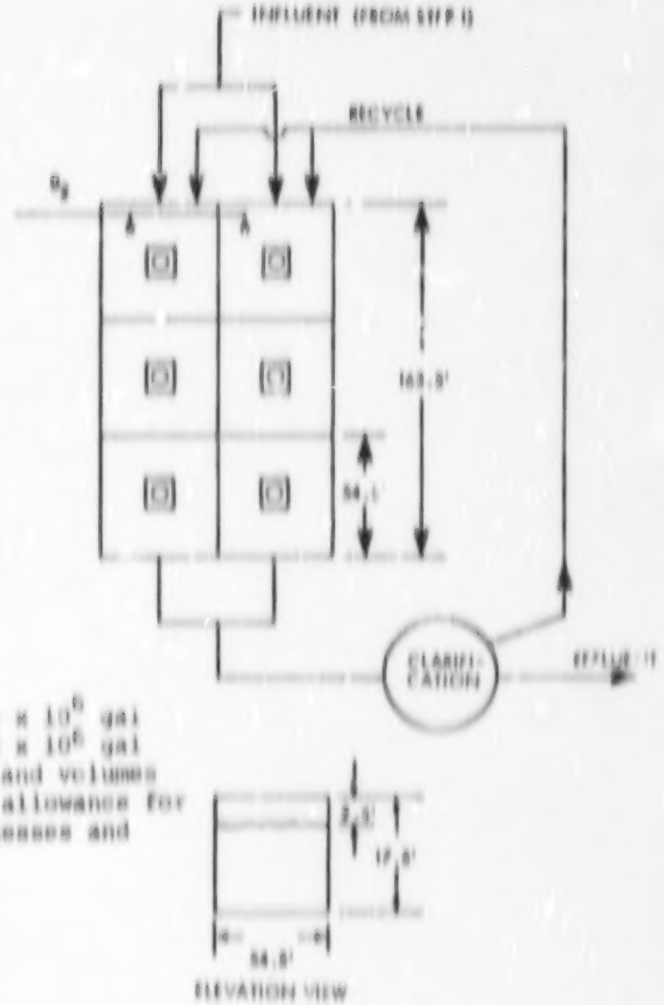
Costs

The costs of the HPOAS system including sludge treatment are summarized on Table 18-12 showing the unit cost on the order of $1.61 per thousand gallons of wastewater treated. It is interesting to note that the total electric power requirement including that for oxygen generation and transfer, about 6,526 kw or 8,752 hp, is slightly less than that for the AAS system


OXYGEN
INFLUENT
40.5'
40.5'
CLARIFICATION
EFFLUENT
TO STEP 2
2.5'
17.5'
40.5'
ELEVATION VIEW

Stage volume 1.264 x 10^6 gal
System volume 9.25 x 10^6 gal
NOTE: Dimensions and volumes include no allowance
for wall thicknesses and weirs.

Figure 10-7. Configuration of step 1 of [illegible] System.



INFLUENT (FROM STEP 1)
RECYCLE
O_2
PIPELINE OXYGEN
163.3'
54.1'
CLARIFI-CATION
EFFLUENT
2.5'
17.5'
54.1'
ELEVATION VIEW

Stage volume 0.33 x 10^6 gal
System volume 2.0 x 10^6 gal
NOTE: Dimensions and volumes include no allowance for wall thicknesses and weirs.

Figure 10-8. Configuration of step 2 of HPOAS System.

TABLE 8-12. COST OF HIGH PURITY OXYGEN ACTIVATED SLUDGE (HPOAS) SYSTEM

Capital Costs	$10^6$$
Equalization	1.19
Step 1 HPOAS:	
Oxygenation Basins	1.96
Clarification	0.25
Cooling Tower	0.08
Pumps for Recirculation	0.13
Step 2 HPOAS:	
Oxygenation Basins	0.65
Clarification	0.29
Pumps for Recirculation	0.02
Oxygenation Equipment & Related Instrumentation for Steps 1 and 2*	3.50
Installation of Oxygenation Equipment & Related Instrumentation*	0.32
DAF Thickening	0.54
Vacuum Filtration	0.36
TOTAL	9.09
Operating Costs	**$10^6$$/yr**
Amortization & other capital-related items @ 15% of capital/yr	1.36
Maintenance:	
Concrete work	0.05
Machinery	0.08
Electricity @ 2,470 Kw**	0.40
Chemicals:	
Phosphorous	0.32
Oxygen, 295 tons/day @ $14.32/ton (see Table (8-13)	1.40
TOTAL	3.61
TOTAL OPERATING COSTS	3.61 $/1000 gal

---

*Quotation from Union Carbide

**Excluding electricity required for oxygen generation

TABLE 18-13. COST OF OXYGEN (MODIFIED FROM REFERENCE 29)

	$/ton
Capital of $13,000/(ton/day) amortized at 15%/yr for 329 days/yr	5.94
Power, 330 kw-hr/ton at 2¢/kw-hr	6.60
Miscellaneous supplies[29]	0.75
Maintenance[29] (2.4% of capital)	0.94
	14.23

---

which was about 9,100 hp. However, the AAS system as shown in Figure 18-1 is not comparable with the HPOAS system in Figure 18-6, as the BOD removal efficiency is much higher for the HPOAS system than for the AAS system being more than 99 percent in the HPOAS system and about 90 percent in the AAS system.

18.7 ACTIVATED TRICKLING FILTER--HIGH PURITY OXYGEN ACTIVATED SLUDGE (ATF-HPOAS) SYSTEM

In the systems considered so far, the capital and energy costs of aeration (or oxygenation) have dominated all other costs. This is not surprising considering the very large amounts of BOD that must be removed. As discussed in Section 18.8, since anaerobic biological treatment is not considered feasible in its present state of development, ways to modify aerobic treatment systems and reduce the capital and energy requirements were sought.

The use of dual biological processes (using a combination of trickling filter and activated sludge) for industrial wastewater treatment is not new.[18] Success in the treatment of wastewaters from organic chemical manufacturing, petrochemical refining and meat processing industries has been reported.[18,19] In most of the reported cases the water contaminants of primary concern have been phenols and BOD, and their highly cost-effective removal can be made possible by successfully combining the desirable attributes of trickling filter and activated sludge processes into the most economical treatment system.[18] Furthermore, in the treatment of refining wastewater it has for more than two decades been found highly economical and desirable to achieve bio-oxidation and water cooling in a cooling tower structure.[22] Functionally, the cooling tower in this case is analogous to the trickling filter in terms of organic removal, although differences exist in their physical configuration and design. We propose merging a trickling filter with a cooling tower as an integral unit prior to the HPOAS. Since the removal of BOD may be more significant than the removal of heat in such an application, the new unit will be designated as an activated trickling filter (ATF). An activated trickling filter as used here is a trickling filter of plastic medium loaded continuously with the mixed liquor from the HPOAS units, as shown in Figure 18-9. The ATF is expected to achieve the following objectives:

(1) Reduce BOD by about 30 percent as a pretreatment to the HPOAS system.

(2) Reduce the temperature of the recycled mixed liquor from the HPOAS system from about 95° to 80°F.

(3) Strip off the excessive carbon dioxide from the recycled mixed liquor.

Qualitatively, the use of an ATF-HPOAS system may be expected to have the following advantages over the use of an HPOAS system alone:

(1) Less energy required. The energy required to pump water and drive the air fans in the ATF may be lower than that to transfer the large quantities of air or to generate and transfer adequate oxygen for the activated sludge process.

(2) Lower capital and operating costs.

(3) Fewer system upsets and higher treatment reliability. This is due to the fact that fixed biological growth is less susceptible to loss of the biota activity through shock loadings of either hydraulic feed, BOD concentration or toxicants. Recycling of the mixed liquor may also contribute to the treatment reliability.

The use of an ATF in combination with an HPOAS system in the manner shown on Figure 18-9 results in an organic loading of about 8,000 lb BOD/(10^3 ft^3 of medium)(day) compared to current practice of having high organic loadings in the range 1,000-1,400 lb BOD/(10^3 ft^3)(day). This occurs because the BOD concentration in the feed water is high and, also,

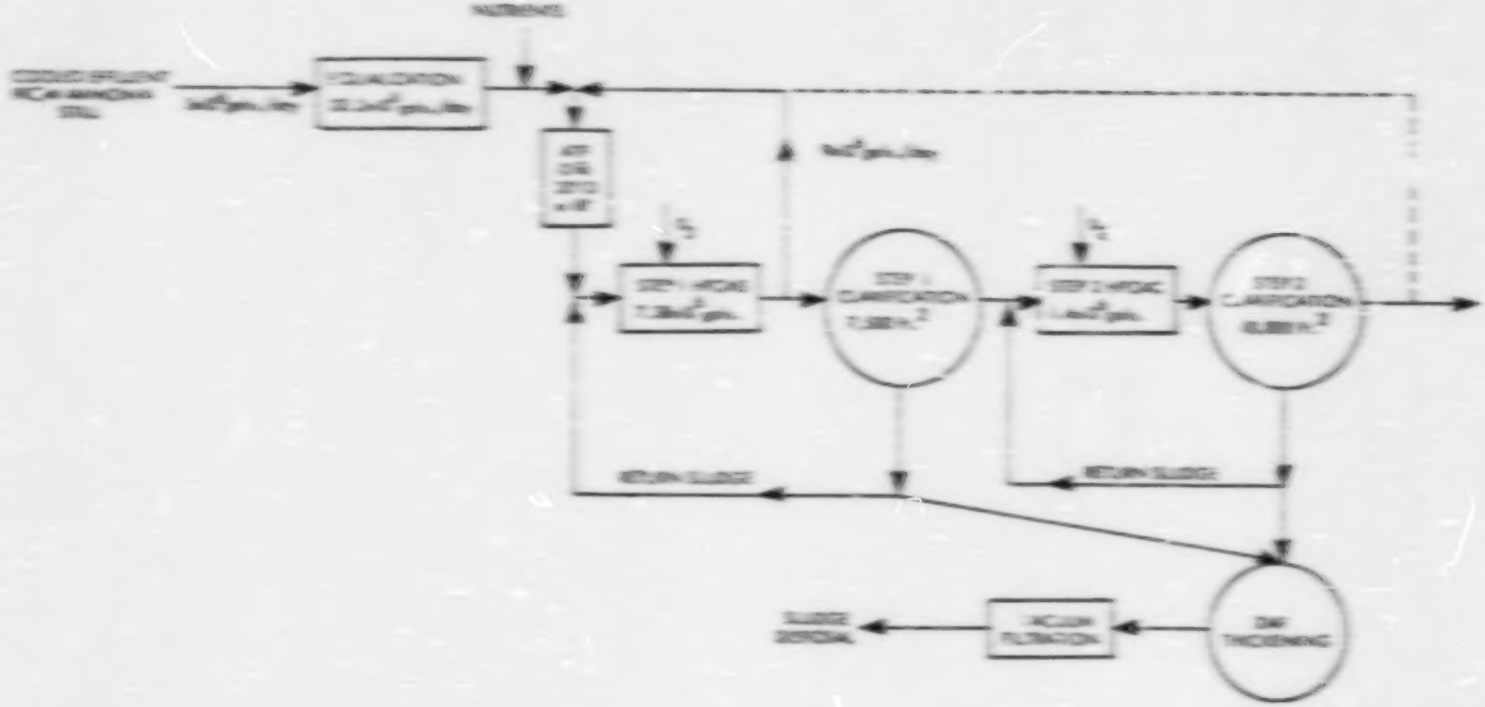

NUTRIENTS
EQUALIZATION
STEP 1 HPOAS
STEP 1 CLARIFICATION
STEP 2 HPOAS
STEP 2 CLARIFICATION
RETURN SLUDGE
RETURN SLUDGE
DAF THICKENING
VACUUM FILTRATION
SLUDGE DISPOSAL

Figure 10-4. Activated trickling filter—high purity oxygen activated sludge system.

because the recirculation rate is determined by the cooling requirement of Step 1 of the HPOAS system and is not adjusted to control the BOD loading of the trickling filter. Also, there are contaminants in the coal conversion wastewater other than phenol which may inhibit biochemical oxidation in the ATF to some extent. For these reasons, as will be seen in the description of the design procedure given below, the usual trickling filter design equation has been modified by assuming that the reduction in BOD obtained is only 30 percent instead of the 80 percent found by use of the standard design equation. Furthermore, forced ventilation is used to avoid oxygen transfer limitation.

The other assumptions that have been made in the design are (1) that first order kinetics prevail in both steps of the HPOAS with 95 percent removal in each step and (2) that without recycle the water temperature would rise 1°F per 200 mg BOD/l removed during passage through Step 1 of the HPOAS system.

According to B.F. Goodrich General Products who manufactures plastic medium for trickling filters, no difficulty is anticipated in running the mixed liquor (MLSS = 6,800 mg/l) through the filter medium as long as the MLSS does not exceed 10,000 mg/l and the diameter of solid particles is less than 0.5 inches. The suspended solids in the effluent from ATF will be effectively removed in the HPOAS process, and the suspended solids content in the effluent from the biological treatment system will be in the range 50 to 500 mg/l.[20] In Section 19 a value of 100 mg SS/l is assumed, and this is filtered or not, as demanded by the downstream use or treatment.

Design

The BOD removal relationship for trickling filters may be stated as

$$\frac{L_e}{L_a} = \exp\left(-\frac{KD}{Q^n}\right) \qquad (4)$$

where

L_e = BOD of the effluent, mg/l

L_a = BOD of the influent, mg/l
K = treatability factor
D = fill depth, ft
Θ = temperature factor, = $1.035^{(T-20)}$, where T = water temperature in °C
J = water flux through the filter, gallons/(min)(ft^2)
n = medium factor

The treatability factor K is a measure of the susceptibility of the wastewater to biological treatment. The medium factor n is a function of the character of the medium, e.g., its specific surface area and geometry, etc., which can affect the contact time between water and biological mass on the surface of the medium.

If the trickling filter effluent is recycled, then the influent BOD L_a may be expressed as

$$L_a = \frac{L_0 + NL_e}{1 + N} \tag{5}$$

where

L_0 = BOD in the raw wastewater before mixing with recycled flow, mg/l
N = recycle ratio = recycle flow/raw water flow

Also, the water flux through the filter J can be expressed in terms of the raw wastewater flow as

$$J = (1 + N)j \tag{6}$$

where

j = raw water flow (flow influent to the system) expressed in gallons/(min)(ft^2 of trickling filter)

Combining Equations (4) through (6) gives

$$\frac{L_0}{L_e} = (1 + N)\exp\left\{\frac{KD\Theta}{\left(j(1+N)\right)^n}\right\} - N \tag{7}$$

For the first calculation, the following numerical values have been used:

$K = 0.045$ for coal conversion wastes

$D = 18$ ft for ease of ventilation

$T = 30°C = 86°F$

$\Theta = 1.035^{10} = 1.41$

$n = 0.5$

The recycle ratio R will be set so as to ensure the correct [illegible] control in Step 1 of the HPOAS as Equation (7) relates the raw water [illegible] gallons/(min)(ft^2) to the fraction of BOD remaining. Since the desired treatment rate in gallons/min is given, Equation (7) relates the desired fractional removal of BOD to the cross-sectional area of the trickling filter.

It should be pointed out that since it is the mixed liquor from Step 1 of the HPOAS being recycled, rather than the filter effluent as used in the derivation of Equation (7), using L_e as the effluent BOD from the ATF will provide a conservative design.

Equation (7) has restrictions. To avoid excessive shear on the biomass, the total flux J should not exceed about 4 gallons/(ft^2)(min) (information from B.F. Goodrich General Products and Reference 22). The flux cannot be very low or distribution of the water over the medium cannot be accomplished. Also, it must be remembered that Equation (7) has been used for a BOD loading of up to 1,000-1,400 lb BOD/(10^{3}ft^3 filter medium)(day) in present practice. Higher BOD loadings will tend to reduce the BOD removal efficiency as oxygen transfer becomes limiting.

To control the undesirable effects of organic overloading, forced draft ventilation will be provided. In the preliminary design modular units of ATF designed for ease of counterflow ventilation, each 20 feet in diameter and 18 feet in height, have been used. The capital cost of each module, including containment structure, filter medium, rotary distribution, fans and installation, is estimated at $50,000.

The design is given on Table 18-14 and is detailed below for the HPOAS and the ATF systems. The results are shown on Figure 18-9.

TABLE 10-14. PRELIMINARY DESIGN CALCULATION OF ACTIVATED TRICKLING FILTERS

% BOD Removed	90	85	80	75	70
L_e/L_0	0.1	0.15	0.2	0.25	0.3
L_0/L_e	10	6.67	5	4	3.33
$\ln\left[\frac{(L_0/L_e) + 3}{4}\right]$	1.18	0.88	0.69	0.56	0.48
j, gpm/sq ft	0.23	0.42	0.68	1.04	1.54
Total hydraulic loading, J = 4j	0.94	1.68	2.72	4.16	6.16
Cross-sectional area required = A, ft^2			3,063		
Medium volume = 18A ft^3			55,134		
Organic loading, lbs BOD in raw-waste per (1,000 ft^3)(day)			8,168		
No. of modular ATF units used			10		

HPOAS System Design

(1) Assume that 30 percent of the BOD will be removed by the ATF and 95 percent of the remaining BOD is removed in Step 1 of the HPOAS; 11,970 mg/l are removed in Step 1.

(2) Design the HPOAS as described in Section 10.6. In particular, find the recycle rate for temperature control. There is 1°F rise for 200 mg BOD/l removed, so the temperature rise in Step 1 is 60°F without recycle. Let R be the recycle rate (10^6 gallons/day) when 3×10^6 gallons/day are processed. The heat evolved which would be enough to heat 3 million gallons through 60°F must only heat (R+3) million gallons through 15°F, so $R = 9 \times 10^6$ gallons/day and the recycle ratio N = 3.

ATF System Design

(1) Assume various percentages of BOD removed and calculate the water flux from Equation (7). The calculations are shown on Table 10-14.

(2) Choose the column in which the total hydraulic loading is less

than, and close to, 4 gpm/ft². This is the column with 80 percent BOD removal.

(3) For the required feed rate (3×10^6 gal/day) find the total cross-sectional area. At 0.68 gpm/ft² this is 3,063 ft².

(4) Find the medium volume noting that a depth of 18 ft is used. The volume is 55,134 ft³.

(5) Find the organic loading based, in this case, on 18,000 mg/l influent BOD = 0.45×10^6 lb BOD/day. The loading is 8,162 lb BOD/(10^3ft³)(day). This loading is six to eight times current practice, and it is assumed that the trickling filter designed here, with forced ventilation included, will produce only a 30 percent reduction in BOD.

(6) Find the number of modular units, each having 314 ft² cross-sectional area and costing $50,000.

In this example it is found that ten modules of ATF will reduce the BOD by 30 percent. This adjustment to 30 percent is an educated guess, and it is considered a conservative estimate in view of the flexibility provided by the ventilation and the recycling of the mixed liquor. The verification of above assumptions can be achieved by pilot studies.

Adjusting the Activated Trickling Filter Design to Different Throughputs and BOD Loadings

The ATF-HPOAS system turns out to be the system of choice among all biotreatment systems in this study. A method of scaling the example to many site-specific plants is therefore needed. This was done as follows:

(1) Equation (7) was used to adjust K, the water treatability factor, to obtain a 30 percent reduction in BOD in the exemplary plant. If in Equation (7) one puts

$\Theta = 1.41°C$

$n = 0.5$

$\phi = 3$

$D = 18$ ft

$j = 0.68$ (from Table 18-14) gal/(min)(ft² of trickling filter)

$L_e/L_0 = 0.7$

then

$$K = 6.6 \times 10^{-3} \ (\mathrm{ft}^{-1})(°\mathrm{C}^{-1})$$

(2) For a requirement of 30 percent reduction in BOD, Equation (7) now becomes

$$\ln\left[\frac{1.43 + N}{1 + N}\right] = \frac{0.1675}{\sqrt{j}\ \sqrt{(1+N)}} \qquad (8)$$

(3) For each design, N is set by the cooling requirement in Step 1 of the HPOAS system. Equation (8) gives the feed water flux, j.

(4) If the total water flux $J = (1+N)j$ exceeds 4 gpm/ft^2, use 4 gpm/ft^2.

(5) The total area of the ATF, the number of modules and the total cost are then calculated as for the example above.

Costs

The costs of the complete system are shown on Table 18-15. Step 1 of the HPOAS consists of five trains, each having five stages of oxygenation reactors. Step 2 consists of one train having four stages in series. The unit cost is about $3.10 per thousand gallons of wastewater treated, 16 percent less than that of the HPOAS system alone (which was about $3.6 per thousand gallons). The total power requirement including that for oxygen generation, oxygen transfer and pumping is about 4,770 kw and is significantly less than that for HPOAS alone, which is about 6,536 kw. It may be concluded with confidence that the use of ATF prior to HPOAS may significantly improve the cost effectiveness of the biological treatment. It should be pointed out that the 30 percent BOD removal by ATF is considered a conservative estimate, as indicated on Table 18-14, and no optimization has been attempted.

The activated trickling filter-high purity oxygen system is the chosen system wherever biotreatment is used in the complete water treatment plant designs of Section 19. For ease in rapid cost estimating, the design and costing procedures detailed above were used to cost the four cases shown on

TABLE 10-15. COSTS OF ACTIVATED TRICKLING FILTER - HIGH PURITY OXYGEN ACTIVATED SLUDGE (ATF-HPOAS) SYSTEM

Capital Costs		$10^6$$
Equalization		1.19
ATF		
Containment Structure	0.10	
Filter Medium	0.14	
Rotary Distributor	0.20	
Ventilation Fans	0.02	
Installation	0.04	0.50
Step 1 HPOAS		
Oxygenation Basin		1.71
Clarification		0.18
Pumps for Recirculation		0.13
Step 2 HPOAS		
Oxygenation Basin		0.47
Clarification		0.20
Pumps for Recirculation		0.02
Oxygenation Equipment and Related Instrumentation for Steps 1 and 2*		3.10
Installation of Oxygenation Equipment and Related Instrumentation*		0.28
DAF Thickening		0.54
Vacuum Filtration		0.36
TOTAL		8.68
Operating Costs		$10^6$$/yr
Amortization and Other Capital-Related Items @ 15% of capital/yr		1.30
Maintenance		
Concrete Work		0.05
Machinery		0.08
Electricity @ 1,930 kw**		0.31
Chemicals		
Phosphorous		0.32
Oxygen, 218 tons/day @ $14.23/ton		1.04
TOTAL		3.10
TOTAL OPERATING COST		$.1/thousand gallons
BOD Removed		224.7 tons/day

---

*Quotation from Union Carbide.

**Excluding energy for oxygen generation.

TABLE 18-16. UNIT COSTS OF BIOLOGICAL TREATMENT
USING ATF-HYGAS SYSTEM

Coal Conversion Process	Water Flowrate 10^3 lbs/hr	Water Flowrate 10^6 gals/yr	Cost of Biological Treatment 10^6 \$/yr	Influent BOD mg/l	BOD Removal 10^6 lbs/yr	Unit Cost \$/lb BOD Removed
Hygas	273	263	0.7	13,000	28.4	0.025
SRC	256	246	1.27	30,000	61.5	0.021
Lurgi-Power	581	556	1.69	18,000	83.3	0.020
Lurgi-Power	1,040	999	3.1	18,000	149.7	0.021

Table 18-16. Except in the Hygas plant, which has a low throughput and the lowest loading, the cost seems to be directly proportional to the BOD removal rate. In Section 19 the costs used are \$0.025/lb BOD removed for the Hygas plants and \$0.021/lb BOD removed in the other plants.

18.8 ANAEROBIC BIOLOGICAL TREATMENT

In the anaerobic biological treatment processes, organic constituents of the wastewater are converted to methane and carbon dioxide. General explanations are given in Reference 23. The significant advantages of anaerobic over aerobic biological treatment are:

(1) Less sludge growth will be produced in the anaerobic process, about 0.05 to 0.2 pounds suspended solids per pound BOD_L, while the corresponding figure for the aerobic process may be as high as 0.4.[17] Variations in the above figure primarily depend on the nature of organic constituents and the solids retention time (SRT).

(2) The problem of biological sludge disposal and the requirement of nutrient, phosphorus in this case, will be significantly reduced.

(3) Elimination of aeration results in significant savings in energy and in the capital and operating costs.

(4) The methane gas produced can serve as a source of fuel.

On the other hand, the major disadvantages of anaerobic processes lie in their relatively high susceptibility to upsets due to toxicants or shock loads and the lack of field experience with the coal conversion wastewater.

The dry solid residue generated through biological treatment will be on the order of 10-20 tons/day, while the total ash generated from the coal conversion facilities may be one hundred times as much, or more. Therefore, the problem of biological sludge disposal is relatively insignificant in coal conversion facilities.

As to the methane generation from anaerobic treatment processes, it is also quantitatively insignificant in comparison with the total gas production from the coal conversion facilities, about 250 million scf/day. Assuming that 90 percent of 30,000 mg/l COD may be converted to methane at 5.61 cubic foot methane per pound of COD, a 10^6 gal/day wastewater plant will be able to produce up to 1.3 million scf/day of methane. While this is small compared to plant production, it is an important part of the plant driving energy and can conveniently be used on site (for example, for drying coal, etc.).

The major advantages of utilizing anaerobic biological treatment for coal conversion wastewater will lie in the cost savings due to the elimination of aeration, consisting of both capital and energy expenditures, and, to a lesser extent, the reduction in nutrient requirements.

As to the disadvantages of anaerobic treatment for coal conversion wastewater, upsets of methane-forming bacteria by toxicants existing in the wastewater or shock loads are probably the most critical considerations. Methane-forming bacteria usually exhibit very slow growth and are relatively sensitive to constituents in the wastewater. Once the anaerobic process suffers an upset, it usually takes weeks or months to have methane-forming bacteria re-established.

The first constituent of concern is phenol if anaerobic processes are used for the treatment of coal conversion wastewater. There have been contradictory reports on the biodegradability of phenol in anaerobic treatment processes. Some researchers have found phenol to be nonbiodegradable (correspondence with Prof. P.L. McCarty and Reference 24), while others indicated that phenol may be used as the sole source of organic carbon and, based on gas production data, at least 75 percent of phenol may be used (correspondence with Prof. J.S. Jeris).

At concentrations exceeding certain levels, phenol will inhibit methane production and thus render the anaerobic process unfunctional. The inhibitory concentration of phenol seems to vary depending on the types of testing conducted. In laboratory studies, 195 mg/l and 300 mg/l of phenol fed to an anaerobic system have been found to be nontoxic. A more recent study[24] showed that for an active methane-producing, unacclimated, domestic digester sludge the 50 percent inhibitory concentration of phenol (based on gas production) was found to be larger than 1,000 mg/l under substrate-limiting conditions, and it ranged from 300 to 1,000 mg/l (averaging about 400 mg/l) under nonsubstrate-limiting conditions. Through acclimation the inhibitory concentration of phenol will increase. Under nonsubstrate-limiting conditions with a phenol concentration of about 500 mg/l, the methane-forming activity of the acclimated biomass was found to be about 95 percent of that for the noninhibited.

In a series of packed-bed anaerobic reactors the effect of four mixed inhibitors, including phenol, formaldehyde, acrylonitrile and ethyl acrylate, was also studied.[24] The mixed inhibitors were found to act synergistically since they were more detrimental to methane formation as a mixture than would have been predicted based on individual chemical inhibition tests.

Acclimation was found[24] to be unsuccessful in a digester-type reactor unless complete mixing was provided. No such problem was observed in the packed-bed type reactor (upflow anaerobic filters). It was also concluded that acclimation in anaerobic systems was at best a slow process and considerable difficulty would likely be experienced in the start-up of a full-scale anaerobic process treating an inhibitory waste.

Other phenolic compounds may be more toxic than phenol to biological treatment processes. For instance, pure cresols have been found to be relatively nontoxic at a concentration of 250 mg/l, while the corresponding concentration for pure phenol has been found to be above 500 mg/l.[10] Furthermore, the large ratio of COD to BOD in the coal conversion wastewater indicates that although phenol constitutes most of the BOD, substantial quantities of other oxygen-demanding substances exist, most of which are probably organic in nature. The effects of these biologically refractory substances on the anaerobic process are unknown at the present time and deserve future study. However, in view of the sensitive nature of anaerobic reactions it is likely that adverse effects on anaerobic reactions may be exerted by these refractory substances.

Based upon the information presently available, if anaerobic treatment is found feasible for coal conversion wastewater the most likely system will probably be in the form of upflow anaerobic filters since it may be more stable than the anaerobic activated sludge or conventional digester systems.[23-26] These different anaerobic systems are schematically shown in Figure 10-10. However, the feasibility and performance of these systems should be fully evaluated by pilot testing before any attempt at preliminary design can be justified. Therefore, for this report no further discussion will be made on anaerobic treatment.

10.9 ADDITIONAL CONSIDERATIONS AND RESEARCH NEEDS

It will be apparent from the discussion on biological treatment that all possible reactor configurations have not been considered and that for those reactors which were considered, some empirical and subjective design procedures had to be used because of a lack of basic information. In this subsection these facts are summed up lest they be forgotten.

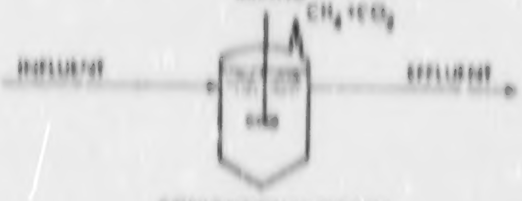
The components of a biological treatment system are:

(1) the wastewater
(2) the biological agents
(3) the treatment reactors.

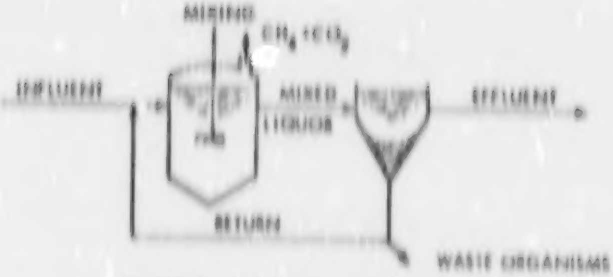
The discussion can conveniently be arranged in this way.

Wastewater

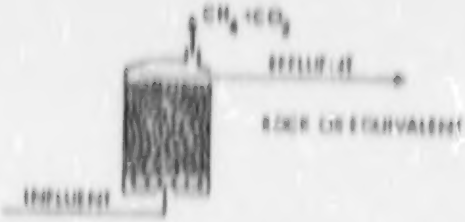
The main consideration here is the biodegradability of wastewater constituents. The use of gross parameters, like BOD, COD and TOC as used above, is not adequate to answer the following key questions which should be studied in future research:


MIXING
$CH_4 + CO_2$
INFLUENT
EFFLUENT
GAS

CONVENTIONAL PROCESS


MIXING
$CH_4 + CO_2$
INFLUENT
MIXED LIQUOR
EFFLUENT
GAS
RETURN
WASTE ORGANISMS

ANAEROBIC ACTIVATED SLUDGE PROCESS


$CH_4 + CO_2$
EFFLUENT
ROCK OR EQUIVALENT
INFLUENT

ANAEROBIC FILTER PROCESS

Figure 10-10. Schematic anaerobic treatment systems (modified from Reference 23).

(1) What constituents are toxic to biochemical degradation, and what are their threshold concentrations?

(2) What is the expected COD and TOC removal by biological treatment?

(3) What are the constituents of the remaining COD and TOC, and what is their fate after biological treatment?

Biological Agents

Most biological agents utilized in wastewater treatment are mixed cultures. With respect to the treatment of coal conversion wastes, the following questions need to be answered:

(1) What is the feasibility of treating coal conversion wastes by anaerobic processes which can result in a very high energy saving?

(2) Are there any specific biological strains that could work more satisfactorily than mixed cultures?

(3) What are the characteristics and environmental requirements of these strains?

(4) What are the values of the fundamental coefficients in the reaction between biological agents and substrates (wastewater), for instance, the coefficients in the Monod model?

Treatment Reactors

In general, for either aerobic or anaerobic treatment processes reactors may be classified according to the mode of biological growth and the medium involved:

(1) suspended growth

(2) fixed-bed growth

(3) fluidized-bed growth

For aerobic treatment, according to the discussion in Section 10.7, the use of a fixed-bed (ATF) appears to be more energy-effective and cost-effective than the use of suspended growth (HPOAS), while the suspended growth tends to provide a better effluent quality than the fixed-bed growth does. A definitive conclusion on such a comparison can only be obtained through pilot studies using actual wastewaters.

The use of a fluidized-bed reactor is not developed enough to have been costed in this study, but it is discussed below.

Tapered Fluidized-bed Bioreactor

Scott *et al.* at Oak Ridge National Laboratory[31] have experimented with the use of a tapered fluidized-bed bioreactor for the removal of phenol. The significant characteristics and findings of this study include:

(1) The experimental bench-scale system utilized fluidized anthracite coal in the particle size range of 0.15 to 0.18 mm.

(2) A mutant strain of *Pseudomonas* bacteria, under the trade name Phenobac, was found superior to mixed cultures from activated sludge system and was used for the experiment.

(3) Synthetic feed solutions made from deionized water and reagent grade of phenol and other additives were used.

(4) The phenol concentration in the feed stream ranges about 20-60 ppm, while the effluent phenol concentration is mostly less than 1 ppm and, in certain instances, less than 25 ppb.

(5) Under the experimental conditions when oxygen transport is not limiting, a multistage tapered fluidized-bed system appears to be at least ten times more efficient than the conventional stirred-tank reactors in terms of the rate of phenol conversion. Thus a significant decrease in reactor volume could be expected with the fluidized-bed system (the difference in cost has not been estimated).

(6) If higher phenol concentration exists in the influent, oxygen transfer will become limiting.

(7) It was observed that the *Pseudomonas* used may be stored at 4°C almost indefinitely for later use, and after *Pseudomonas* is reintroduced into the bioreactor the system will be ready for normal operation in a very short time.

(8) The use of fluidized-bed bioreactors alleviates operational problems associated with biomass build-up and allows easy removal or addition of the active materials.

(9) The tapered reactor tends to stabilize the fluidized bed while allowing a much wider range of operating conditions, namely, flow variations.

According to the information outlined above, tapered fluidized-bed bioreactors appear to be a promising system to provide polishing treatment to ensure an effluent phenol concentration below 1 mg/l or less. However, in order to improve biological treatment of coal conversion wastes, further research on tapered fluidized-bed bioreactors is needed in the following areas:

(1) Pilot testing of tapered fluidized-bed bioreactors to obtain design information, using actual coal conversion wastewater rather than synthesized feed solutions.

(2) Aerobic biological treatment of high-strength phenolic wastes may well be limited by oxygen transfer rather than being limited biokinetically. Therefore, the oxygen limitation should be fully characterized and means determined to circumvent it.

(3) The fact that a mutant strain of Pseudomonas may be stored and used more effectively than mixed cultures from activated sludges deserves further characterization, probably involving the determination of various fundamental coefficients in the biochemical transformation reaction.

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SECTION 19

SITE STUDIES - 2: WATER TREATMENT PLANTS

19.1 INTRODUCTION AND CONCLUSIONS

The study is divided into three sections by location, which fixes the assumed water supply and quality. The first part of the study is concerned with plants located in North Dakota. The water supply is adequate, cheap and clean. Because of this, reasonably generous amounts of water are evaporated for cooling; in all cases the cooling tower makeup rate is several times the plant effluent condensate rate. The foul condensate only has to be treated to a suitable quality for the cooling towers or for disposal as dust control and ash sluice water. Discussion centers on the cooling tower, the largest water consumer. The assumption of a high chloride concentration in process condensate leads to the special requirement of desalting this water for the power plant.

In New Mexico the source water is assumed to be brackish. Therefore cooling water consumption is reduced from the consumption in North Dakota. Most of the discussion concerns where and how to apply desalting technologies.

In Wyoming, source water is assumed to be very scarce allowing the study of an exemplary plant in which foul condensate, or sewage from the satellite town, should be treated for feed to a boiler.

Various schemes are considered. For the schemes selected the approximate costs (expressed as $\$/10^6$ Btu of product fuel or ¢/kw-hr) are given on Table 19-1 along with the heat and electricity requirements. A word is needed about accuracy. The costs in this report are minimum; they do not include engineering fees or other than the bare minimum investment cost; land cost is omitted as is all site preparation and most foundation work;

TABLE 19-1. APPROXIMATE COST AND ENERGY REQUIREMENTS FOR TOTAL PLANT WATER TREATMENT

	Approximate Cost*		Approximate Energy**		
	$/hr	$/$10^6$ Btu product fuel or ¢/kw-hr power	10^6 Btu/hr	kw	% Product Energy
Hygas					
North Dakota	287	0.028	67	640	0.74
New Mexico	404	0.040	67	2290	0.93
Wyoming	291	0.029	67	665	0.74
Synthane					
Wyoming	664	0.066	136	2800	1.7
SRC					
North Dakota	216	0.016	[illegible]	1670	0.75
New Mexico	185	0.014	56	1823	0.58
Wyoming	302	0.022	124	--	0.92
Electric Power					
North Dakota	835	0.084	230	3750	2.7
New Mexico	774	0.077	150	5650	2.1
Wyoming	566	0.057	170	2170	1.9

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*Approximate operating plus amortized capital costs with credit taken for sale of ammonia.

**Total energy is sum of steam and electricity converted at 10,000 Btu/kw-hr in power plants and 11,700 Btu/kw-hr in gas and SRC plants.

there is no allowance for a control building or laboratory. In operating costs the labor, laboratory and overheads have been omitted. However, the costs are quite good enough to distinguish between alternatives, which is the major purpose. A maximum cost for operating the overall water treatment plant will not exceed three times the numbers of Table 19-1 and will probably cluster around twice the numbers of Table 19-1.

As a process was moved from site to site, very different qualities and quantities of intake water were assumed. In spite of this the maximum cost variation from site to site is 1.7 times for SRC and 1.4 times for Hygas and power plants. The cost is unlikely to exceed 5 percent of the sale price of the product fuel for any of the plants.

In the Hygas process, boiler feed water treatment is 31 to 32 percent of the total water treatment cost in North Dakota and Wyoming. However, in New Mexico, with a brackish water intake, the desalting costs including boiler feed are 49 percent of the total. The brackish intake water makes the cost in New Mexico higher than the cost of the other two sites.

For SRC, Power and Synthane, the cost of boiler feed water treatment is in the range 11 to 23 percent of the total water treatment cost at North Dakota and Wyoming; at New Mexico the cost of desalting plus boiler feed treatment is 41 to 46 percent of the total. However, for these processes other things affect the cost even more and the added cost of desalting is swamped by other factors (discussed in later sections).

The cost of water treatment for the Synthane plant at Wyoming is higher than for the Hygas plant at the same site. When compared to Hygas, the Synthane process is assumed to put out about twice the foul condensate and to have about twice the concentration of contaminants. As a result, 60 percent of the difference is in the biotreatment and the rest is in other treatments applied to foul condensate. A fourfold increase in contaminant load may not occur, but if it does it will increase water treatment costs at least twofold.

Water treatment cost for power plants which employ Lurgi technology is higher than for the fuel production plants. Note that the units used in Table 19-1, namely $/10^6 Btu and ¢/kw-hr, are comparable: about 10,000 Btu are used to make 1 kw-hr. However, power plants have only half the efficiency of fuel plants, so water costs based on product energy will be doubled by this fact alone. Furthermore, the higher fuel condensate effluent rate caused by an intake of wet coal to the Lurgi gasifiers will tend to raise costs over those in a gas producing plant using dry coal. Costs in North Dakota and New Mexico hardly differ and are higher than in Wyoming, because desalting is needed at both of the first two sites. In North Dakota chloride is introduced in the coal and in New Mexico salt is introduced in the source water.

In considering the energy requirements it should be noted that the direct steam used, tabulated as 10^6 Btu/hr in Table 19-1, is never less than 2.5 times the steam needed to generate the electricity also tabulated. Since desalting technologies, reverse osmosis and electrodialysis use electricity and not direct steam, it is apparent that salt removal plays only a small part in energy consumption. In fact, the energy required is very much controlled by the energy for ammonia separation which is directly proportional to the rate of production of foul condensate. Whereas sale of ammonia can offset cost, there is no offsetting factor to obscure the importance of this treatment in energy consumption. In SRC plants where foul condensate has a particularly high contaminant concentration, biotreatment, solvent extraction and evaporation add importantly to the energy load.

In designing the fuel plants we had to decide how much electricity to generate on site. The two big users of electricity are the circulation pumps for the acid gas adsorption liquid and the water treatment plants. In all the plants, adequate electricity seems to have been produced. In the Hygas plants 27,350 kw were generated and 8,440 kw were used for the acid gas removal area. In the Synthane plant 31,000 kw were generated and 9,000 kw were used for acid gas removal. In the SRC plants 10,250 kw were generated and 2,300 to 3,400 kw were used for acid gas removal. It would certainly be an improvement to vary the electricity generated with the electricity needed for water treatment, but this would not alter the plant efficiencies very much.

In the gas plants about 300 × 10^6 Btu/hr were allowed for wastewater treatment and other unspecified uses. This seems adequate. In the SRC plants 160 × 10^6 to 220 × 10^6 Btu/hr were allowed, which also seems adequate.

In the power plants 1.4 to 1.8 percent of the coal feed is allowed for wastewater treatment. This is about 4.2 to 5.4 percent of the electricity generated and is adequate.

19.2 PLANTS IN NORTH DAKOTA

Hygas

The Hygas plant uses dry coal and has a low rate of foul condensate effluent. Furthermore, this effluent is not expected to be high in phenol, so extraction of phenol is not likely to pay for itself. The water management schemes shown on Figures 19-1 to 19-3 have been studied. The first difference is in details around the cooling tower. In fact, as will first be shown, Scheme 2 is probably preferred. In Scheme 1 the wastage of biocides and anticorrosion chemicals in cooling tower blowdown is too expensive.

Consider, first, the cooling tower treatment for Scheme 1. An analysis of biotreatment effluent water is required and the analysis is shown on Table 19-2. The total makeup water = 1071 × 10^3 lb/hr. The desired concentration ratio between makeup and blowdown (desired cycles of concentration) = 1071/281 = 3.8. The analyses of various waters are shown on Table 19-3. The source water must be acidified to remove bicarbonate (see Section 15.6 for discussion). The ammonia is assumed not to concentrate because it is volatile.

TABLE 19-2. ASSUMED ANALYSIS OF BIOTREATMENT EFFLUENT WATER

	mg/l			mg/l
Suspended solids	100	PO_4		15
Ca^{++}	*	NH_3		20
Na^+	*	Cl^-	in North Dakota	1200
Mg^{++}	15		in New Mexico	200
HCO_3^-	40		in Wyoming	600
$SO_4^=$	0			

In North Dakota, and probably in Wyoming, much of the chloride enters biotreatment in the form of NH_4Cl. As ammonia is consumed in the biotreatment, lime or soda ash will be added to neutralize the chloride. The concentration of Ca^{++} and Na^+ will depend on the choice of treatment. A nominal concentration of 20 mg/l Ca^{++} has been assumed.

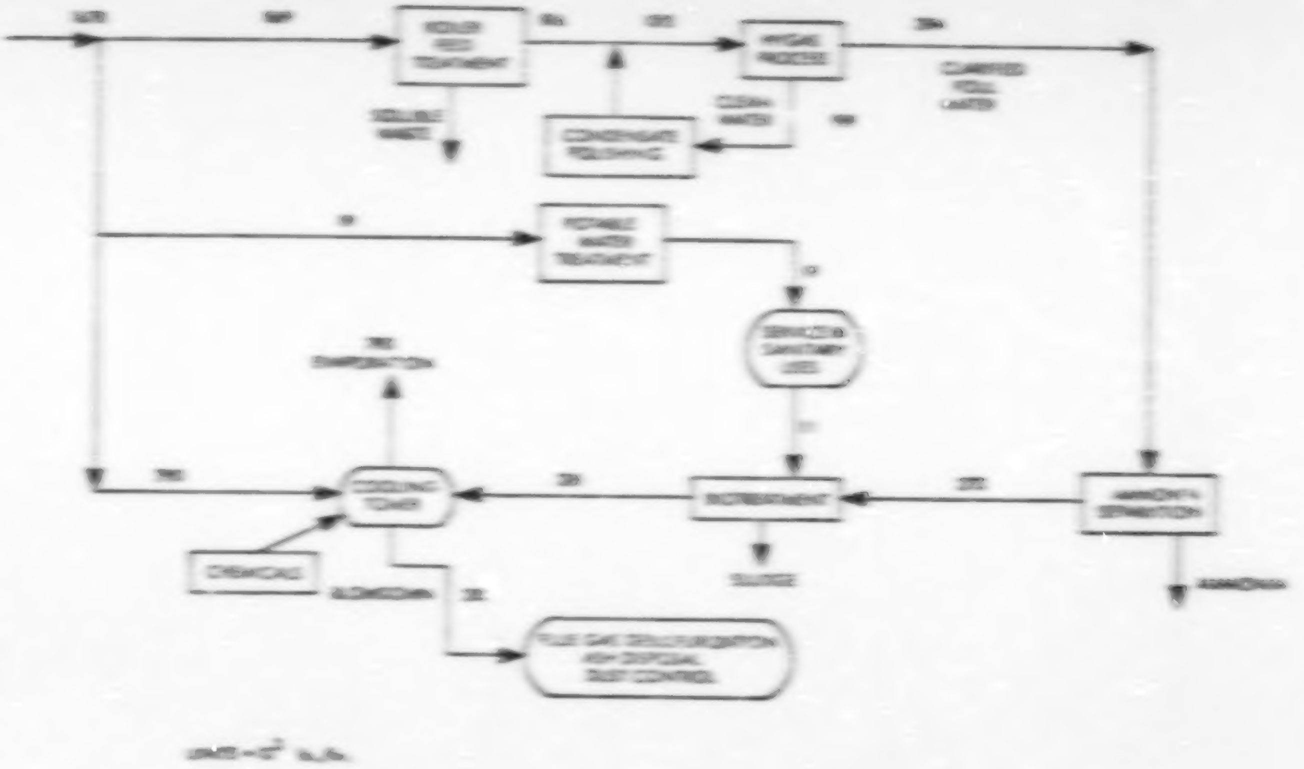
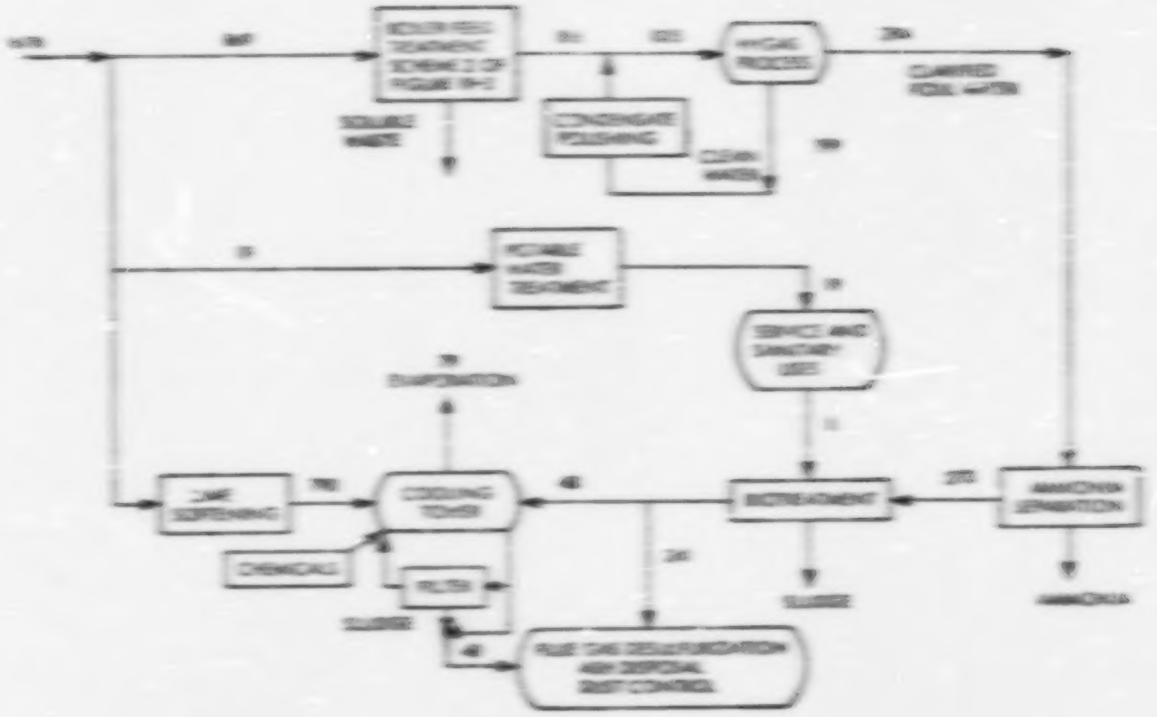
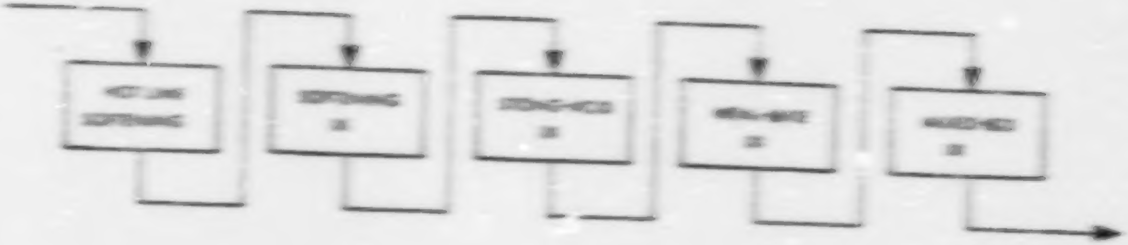

BOILER FEED TREATMENT
SOLUBLE WASTE
HYGAS PROCESS
CLEAN WATER
CONDENSATE POLISHING
CLARIFIED FOUL WATER
POTABLE WATER TREATMENT
SERVICE & SANITARY USES
EVAPORATION
COOLING TOWER
CHEMICALS
BLOWDOWN
BIOTREATMENT
SLUDGE
AMMONIA SEPARATION
AMMONIA
FLUE GAS DESULFURIZATION ASH DISPOSAL DUST CONTROL
UNITS-10^3 lb/h

Figure 19-1. Water treatment plant block diagram for Hygas process at North Dakota (Scheme 1).

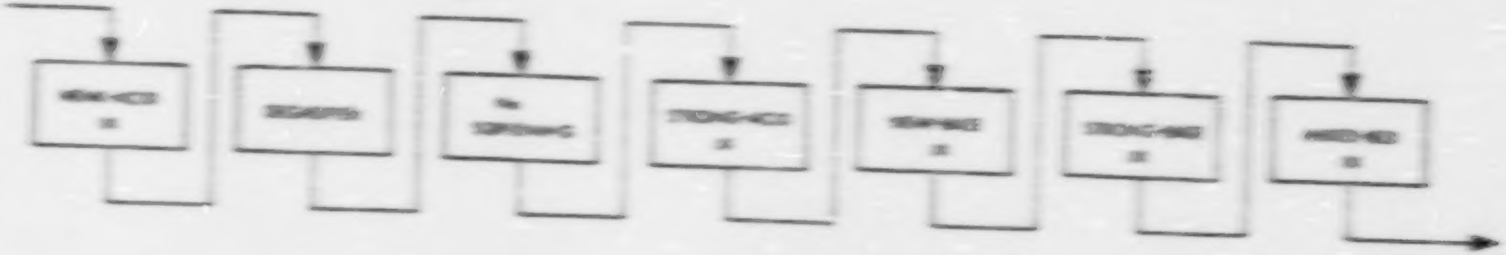

WATER
BOILER FEED TREATMENT SCHEME 2 OF FIGURE 19-1
SOLUBLE WASTE
CONDENSATE POLISHING
HYGAS PROCESS
CLARIFIED FOUL WATER
CLEAN WATER
POTABLE WATER TREATMENT
SERVICE AND SANITARY USES
EVAPORATION
LIME SOFTENING
COOLING TOWER
BIOTREATMENT
AMMONIA SEPARATION
CHEMICALS
FILTER
SLUDGE
SLUDGE
AMMONIA
FLUE GAS DESULFURIZATION ASH DISPOSAL DUST CONTROL

UNITS = 10^3 lb/h

Figure 19-2. Water treatment plant block diagram for Hygas process at North Dakota (Scheme 2).


HOT LIME SOFTENING
SOFTENING IX
STRONG-ACID IX
WEAK-BASE IX
MIXED-BED IX

SCHEME 1


WEAK-ACID IX
DEGASIFIER
Na SOFTENING
STRONG-ACID IX
WEAK-BASE IX
STRONG-BASE IX
MIXED-BED IX

SCHEME 2

Figure 19-1. Boiler feed water treatment schemes in North Dakota.

TABLE 19-1. ANALYSIS OF COOLING TOWER STREAMS FOR HYGAS IN NORTH DAKOTA, SCHEME 1, FIGURE 19-1

	Source Water	Biotreatment Effluent	Source Water After Acidification	Mixed Makeup	Circulating Water at 3.8 Cycles
Flow (10^3 lb/hr)	790	281	790	1071	
	mg/l	mg/l	mg/l	mg/l	mg/l
SS	2	100	2	28	245*
Ca	49	650	49	207	790
Mg	19	15	19	18	68
HCO_3	180	40	0	10	38
SO_4	170	0	312	230	874
Cl	9	1200	9	321	1220
SiO_2	7	0	7	5	19
PO_4	0	15	0	4	15
NH_3	0	20	0	5	5

---

*See text.

The following calculation gives the suspended solids in the circulating water. Let x be the concentration in mg/l. Then the material balance is

$$\frac{x}{10^6} \times 281 \times 10^3 \text{ lb/hr blowdown} = \frac{26}{10^6} \times 1071 \times 10^3 \text{ lb/hr in makeup}$$

$$+ \frac{0.052 \text{ lb dust from air}}{10^3 \text{ lb water evaporated}} \times 790 \times 10^3 \text{ lb evaporated/hr}$$

so x = 245. The circulating water is below all the limits given on Table 14-15. The treatment cost is chemicals only and is given on Table 19-4.

Now consider the cooling tower treatment for Scheme 2, Figure 19-2. First we find what limits the concentration of acidified source water (analysis given on Table 19-3) using the limits on Table 14-15. The limits are:

$$\text{silica (mg/l):}\quad 150/7 = 21.4 \text{ times}$$

$$\text{Mg} \times \text{SiO}_2 \text{ (mg/l):}\quad \sqrt{(60{,}000/19 \times 7)} = 21.2 \text{ times}$$

$$\text{Ca} \times \text{SO}_4 \text{ (as CaCO}_3\text{):}\quad \sqrt{\left[2.5 \times 10^6/(49 \times 2.5)(312 \times 1.04)\right]} = 7.9 \text{ times}$$

TABLE 19-4. COST OF COOLING WATER CHEMICALS FOR HYGAS IN NORTH DAKOTA, SCHEME 1, FIGURE 19-1

	$/hr
H_2SO_4: $\frac{0.8 \text{ lb}}{\text{lb HCO}_3} \times \left(\frac{180}{10^6} \times 790 \times 10^3 \frac{\text{lb HCO}_3}{\text{hr}}\right) \times \frac{\$.036}{\text{lb}}$	4.1
Biocide: Assume \$1/10³ gallons of blowdown because of high concentration of phosphate and carbon: ($\$1/10^3$ gallons) × (1 gallon/8.33 lb) × (281×10^3 lb/hr)	33.7
Anticorrosion chemicals: at $\$0.5/10^3$ gallons blowdown	16.9
Suspending agent: Assumed not required	--
Total:	54.9 $/hr

The concentration is limited by calcium sulfate. To restrict blowdown to conserve chemicals, a cold lime softening will be used on the source water. As described in Section 15.6, lime is added to raise the pH to 9.5 to 10.0. This reduces Ca to about 12 mg/l, HCO_3 to a low level and Mg to about 4 mg/l. Mg in excess of that equivalent to HCO_3 is not removed. Some silica is removed, but need not be estimated because the water is now limited to 21 times concentration by $CaSO_4$. This is the system shown on Figure 19-2. The water analyses are given on Table 19-5.

Note that for Scheme 2 it was necessary to neutralize excess chloride in biotreatment with soda ash to limit the concentration of calcium (see note at the bottom of Table 19-2). For Scheme 1, lime could be used. Lime costs about $1/lb equivalent and soda ash costs about $2.12/lb equivalent, so lime is preferred where permitted. The total cost for neutralizing the biotreatment depends on the analysis which is not known but will not exceed $9.50/hr for lime or $20.10/hr for soda ash, neither of which is large. The difference in cost is much less than the difference between Schemes 1 and 2.

The side stream rate is somewhat more than that needed to remove dust taken in from the atmosphere = 0.052 × 790 = 41 lb/hr. If the side stream filter reduces the concentration from 300 mg/l to 100 mg/l, the side stream rate is

$$(41\ \text{lb dust/hr}) \times (10^6/200\ \text{lb water/lb dust}) = 205{,}000\ \text{lb/hr}$$

$$= 410\ \text{gal/min}$$

The costs are shown on Table 19-6. Scheme 2 is apparently cheaper than Scheme 1. Although approximate costs are used it does seem that using cooling tower blowdown for ash disposal, etc., may not be correct because this procedure wastes chemicals which are expensive because they must be nontoxic.

For boiler feed water treatment the two schemes shown on Figure 19-3 are considered. In Scheme 1, Ca^{++}, Mg^{++}, HCO_3^- and SiO_2 are removed in a hot lime treatment. This is followed by Na^+-Ca^{++} exchange on a softening resin. The silica and hardness are now low enough, but sodium has been increased. Demineralization is carried out in a strong acid exchange followed by a weak

TABLE 19-5. ANALYSES OF COOLING TOWER STREAMS FOR HYGAS IN NORTH DAKOTA, SCHEME 2, FIGURE 19-7

	Source Water After Lime Softening	Biotreatment Effluent	Mixed Makeup	Circulating Water at 21 Cycles
Flow (10^3 lb/hr)	790	40	830	--
	mg/l	mg/l	mg/l	mg/l
SS				100*
Ca	12	20	12	260
Mg	4	15	4.5	95
HCO_3	~ 0	40	2	42
SO_4	170	0	162	3400
Cl	9	1200	66	1386
SiO_2	7	0	7	147
PO_4	0	15	1	21
NH_3	0	20	1	1

---

*Limited by side stream clarification.

TABLE 19-6. COST OF COOLING WATER TREATMENT FOR HYGAS IN NORTH DAKOTA, SCHEME 2, FIGURE 19-1

		$/hr
Lime clarifier for 790 × 10^3 lb/hr: 1,580 gpm Install two clarifiers at 65% capacity costing $520,000; at 17%/yr for 8000 hrs/yr		11.1
Side stream filter for 500 gpm at $150/gpm		1.6
Chemicals:		
Lime	2.5	
Biocide at $0.50/10^3 gallons of blowdown	2.4	
Anticorrosion chemicals	2.4	
Flocculation chemicals	1.6	
Dispersant chemicals	0.7	9.6
Total:		22.3

base exchange followed by a mixed bed. In Scheme 2 the water is first treated with a weak acid ion exchange resin to remove Ca^{++}, Mg^{++} and some Na^+, and to replace these ions with H^+. The hydrogen ions release CO_2 from HCO_3^-, which is removed in the degasifier. Additional removal of Ca^{++} is required on a softening resin. Demineralization requires a strong acid resin followed by a weak base resin. A strong base resin is used for removal of SiO_2 and a mixed bed system is used for final polishing.

Scheme 2 makes more efficient use of regeneration chemicals and is the cheaper. A return condensate polishing system will be required, but this is inexpensive. Compositions of Scheme 2 are shown on Table 19-7.

The treatment shown as Scheme 2 of Figure 19-3 costs about $3.2 × 10^6 (quotation from Permutit) or $64/hr including resin replacement. Regeneration requires 314 lb H_2SO_4/hr, 148 lb NaOH/hr and 94 lb NaCl/hr and costs $26/hr.

The total system cost and energy requirements as entered on Table 19-1 may now be determined for Scheme 2.

Ammonia separation from Figure 16-4 for 0.847 × 10^6 gallon/day costs

TABLE 19-7. BOILER FEED WATER COMPOSITIONS IN NORTH DAKOTA

	After Weak Acid IX and Degasifier mg/l	After Softening mg/l	After Strong-Acid Weak-Base Demineralization mg/l	After Strong-Base IX Silica Removal mg/l
Ca + Mg	20	0	0	0
Na	63	91	4	4
Cl	9	9	0	0
HCO_3	0	0	0	0
SO_4	170	170	2	0
SiO_2	7	7	7	< 1

$4.35/thousand gallons = $154/hr. About $78/hr is recovered from sale of ammonia. At 1.7 × 10^6 Btu/thousand gallons the energy required is 60 × 10^6 Btu/hr.

Biotreatment costs $0.025/lb BOD removed and requires (1900 Btu + 0.18 kw-hr)/lb BOD removed. 13,000 mg BOD/l are removed from 273 × 10^3 lb water/hr, so the cost is $89/hr; the steam required is 7 × 10^6 Btu/hr and the electrical consumption is 640 kw.

Potable water treatment is probably simple chlorination at an insignificant cost.

Total cooling water treatment, including extra for soda ash in biotreatment, costs $32/hr and the energy requirement is small.

Total boiler feed water treatment cost is $90/hr and the energy requirement is small.

These numbers are summed up below.

	$/hr	10^6 Btu/hr	kw
Boiler feed treatment	90	--	--
Cooling water treatment	32	--	--
Ammonia separation	76	60	--
Biotreatment*	89	7	640

---

*In all plants the cost of biotreatment includes sludge dewatering.

Electric Generation

Because the Lurgi process accepts wet coal, the foul condensate rate in this plant is nearly four times the rate in the Hygas plant. We have, however, continued to assume a chloride concentration of 1200 mg/l in the foul water, the same concentration as is assumed at the Hygas and SRC plants. Because these plants consume comparable amounts of coal and coal is the source of chloride, it should be the mass flow of chloride in the foul condensate and not the concentration which is constant from plant to plant. In taking a constant concentration it can be said that the coal composition has been changed. The chloride passes through the ammonia separation and biotreatment untouched and there are important consequences which make the choice of 1200 mg/l chloride an interesting example to study. If the blowdown from the cooling tower is disposed of with ash and for dust control, then 228×10^3 lb water/hr are required. Since the evaporation rate is 2470×10^3 lb/hr, 11.8 cycles of concentration are necessary. This results in an excess chloride concentration in the circulating cooling water. Other ways to use the biotreated effluent for solids disposal and cooling were also considered and it was found the removal of chloride is necessary no matter what scheme is envisaged.

Reverse osmosis has been chosen as the desalting procedure because there is a good probability of simultaneously removing some organic molecules. Prefiltration, with addition of flocculating agents, will be necessary. Reported experience on biotreated municipal waste suggests that membrane fouling can be coped with. The costs assume a two-year membrane life. Precipitation of calcium phosphates can be prevented by addition of a sequestering agent; the costs include a charge for chemicals. As shown on Table 19-2, in the water leaving the process the chloride is mostly in the form of NH_4Cl. In biotreatment ammonia is converted and lime will have been added to prevent the solution from going acid. Therefore, the most important material in the bio-effluent is $CaCl_2$. The total dissolved solids is about 2000 mg/l going into reverse osmosis. Calcium rejection is better than 99 percent by most membranes and electroneutrality encourages the rejection of chloride associated with calcium. An overall rejection of 97 percent of the TDS is quite likely.

Residual ammonia is an exception; ammonia passes most membranes.

Taking a 95 percent recovery of water and a 97 percent point rejection, the exit concentration in the concentrate stream is

$$(\text{feed concentration}) \times 20^{0.97} \;=\; 36{,}600 \text{ mg/l TDS}$$

By material balance the treated water should contain about 180 mg/l TDS. A probable composition of the treated water is

	mg/l
S.S.	0
Ca	50
Cl	86
Si	< 1
NH_3	20
Others	< 1

This is very good quality water.

If effluent from reverse osmosis is mixed with acidified lake water (acidified to remove the high bicarbonate level) and the blend is fed to the cooling tower, the desired concentration cannot be achived because of the limit on calcium sulfate. Lime softening of lake water is required, as it was in Scheme 2 for Hygas. Because side stream clarification will be required for dust removal, the same clarifier can be used for softening. All this leads to the first practical scheme shown on Figure 19-4.

The boiler feed water treatment, not detailed on Figure 19-4, is the same as for Hygas (i.e., Scheme 2 of Figure 19-3) except that mixed bed demineralization is not required. Effluent from the reverse osmosis may be better than lake water as a source for boiler feed, so Figure 19-5 is an obvious alternative. The boiler feed treatment in Figure 19-5 will have to include some scheme for removal of residual dissolved carbon, probably carbon adsorption.

The choice between Scheme 1 and Scheme 2 will be made by knowing which of the treated waters behaves better in the boiler, and without experimental

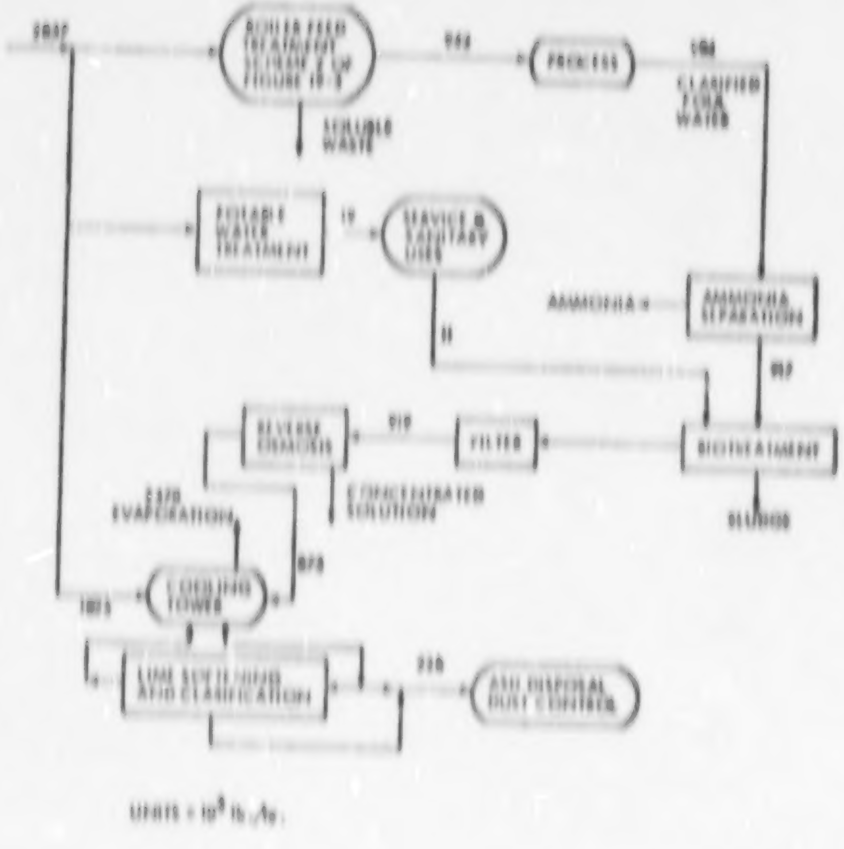

5807
BOILER FEED TREATMENT SCHEME 2 OF FIGURE 19-3
968
PROCESS
194
CLARIFIED FOUL WATER
SOLUBLE WASTE
POTABLE WATER TREATMENT
15
SERVICE & SANITARY USES
AMMONIA
AMMONIA SEPARATION
11
957
REVERSE OSMOSIS
919
FILTER
BIOTREATMENT
CONCENTRATED SOLUTION
SLUDGE
2370
EVAPORATION
879
1875
COOLING TOWER
LIME SOFTENING AND CLARIFICATION
220
ASH DISPOSAL DUST CONTROL
UNITS = 10³ lb./hr.

Figure 19-4. Water treatment plant block diagram for electric generation at North Dakota (Scheme 1).

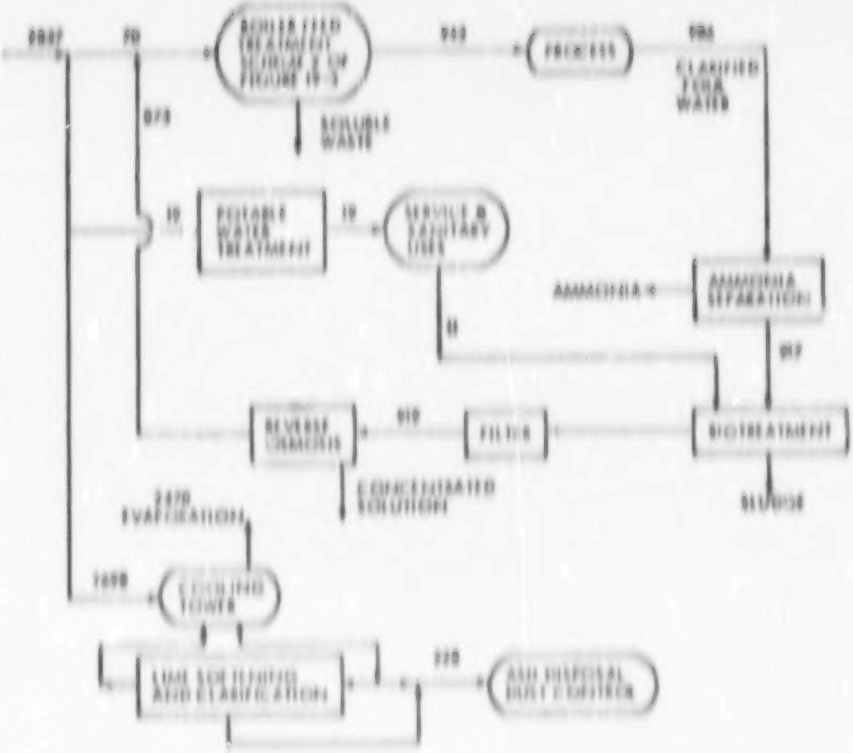

BOILER FEED TREATMENT SCHEME 2 OF FIGURE 19-3
PROCESS
SOLUBLE WASTE
POTABLE WATER TREATMENT
SERVICE & SANITARY USES
AMMONIA
AMMONIA SEPARATION
REVERSE OSMOSIS
FILTER
BIOTREATMENT
CONCENTRATED SOLUTION
SLUDGE
EVAPORATION
COOLING TOWER
LIME SOFTENING AND CLARIFICATION
ASH DISPOSAL DUST CONTROL
UNITS = 10³ lb./hr.

Figure 19-5. Water treatment plant block diagram for electric generation at North Dakota (Scheme 2).

results on reverse osmosis this is not known. Any difference in cost between the schemes cannot be found at our level of accuracy.

The total system cost and energy requirement, as entered on Table 19-1, has been determined for Scheme 1 as follows.

Ammonia separation from Figure 16-4 at 2.8×10^6 gallons/day costs $\$4/10^3$ gallons = \$473/hr. About \$260/hr are recovered from sale of ammonia. At 1.7×10^6 Btu/thousand gallons the energy required is 198×10^6 Btu/hr.

Biotreatment costs \$0.021/lb BOD removed. For 917×10^3 lb/hr with 18,000 mg/l BOD removed, the cost equals \$346/hr. Per pound of BOD removed the energy requirements are 1,900 Btu plus 0.18 kw-hr, so the energy required is 31.4×10^6 Btu/hr plus 2,970 kw.

Potable water treatment is probably simple chlorination at an insignificant cost.

Filtration, with a capital cost of \$75/gpm, a flow of 1.9×10^3 gal/min, a charge of 17%/yr for amortization and maintenance plus flocculating chemicals at 3¢/thousand gallons costs \$6/hr. The energy requirements are small.

Reverse osmosis for 2.6×10^6 gallons/day costs \$132/hr. The energy required is 7.2 kw-hr/thousand gallons, or 780 kw.

The cooling tower side stream clarifier must handle $1,210 \times 10^3$ lb/hr to maintain bicarbonate at an acceptable level. Lime is added only to precipitate bicarbonate. The cost of the clarifier plus lime is \$15/hr. The energy requirement is small.

Cooling tower chemical charges are biocide at \$0.50/thousand gallons of blowdown, corrosion-resistant chemicals at \$0.30/thousand gallons of blowdown (this involves the assumption that side stream treatment with lime does not remove the anticorrosion chemicals; should this not be true then two separate clarifiers should be used: one in the makeup stream using lime and one in the sidestream for dust removal without lime addition), and dispersant chemicals at \$0.03/thousand gallons of side stream. The total cost for cooling water chemicals is \$31/hr.

The boiler feed treatment costs about $\$1.2 \times 10^6$ or \$92/hr for capital, replacement resin and regenerating chemicals. The energy requirement is small. The numbers are summed up below.

	$/hr	10^6 Btu/hr	kW
Boiler feed treatment	94	--	--
Cooling water treatment	46	--	--
Filtration and reverse osmosis	138	--	780
Ammonia separation	213	198	--
Biotreatment	146	31	2970

Alternative for Lurgi Technology

The scheme chosen in this study is not the scheme usually presented in the literature. It is usually stated that for Lurgi plants the foul water, after solvent extraction and ammonia distillation, can be fed to the cooling towers without further treatment (see, for example, Reference 1). From Table IV-1, assuming a 93 percent recovery of phenol with phenol at 6,000 mg/l in the feed, the cost of solvent extraction is $363/hr and the energy required is 110 × 10^6 Btu/hr. About 5,700 lb phenol/hr are recovered, and if this can be sold at 2.2¢/lb, $125/hr is recovered.

Because of the high chloride content it must be assumed that solvent extraction and ammonia separation, without biotreatment, make the water fit for feed to reverse osmosis. If this is true then biotreatment could be eliminated saving $330/hr and 66 × 10^6 Btu/hr (including the steam needed to generate the electricity required for biotreatment).

The alternative route apparently costs 72 percent of the route of Scheme 1 and requires 167 percent of the energy. This difference is probably not due to the low accuracy of cost estimating, and it is worthwhile considering solvent extraction and dropping biotreatment. The technological feasibility of this change requires experimental verification.

Residual Disposal

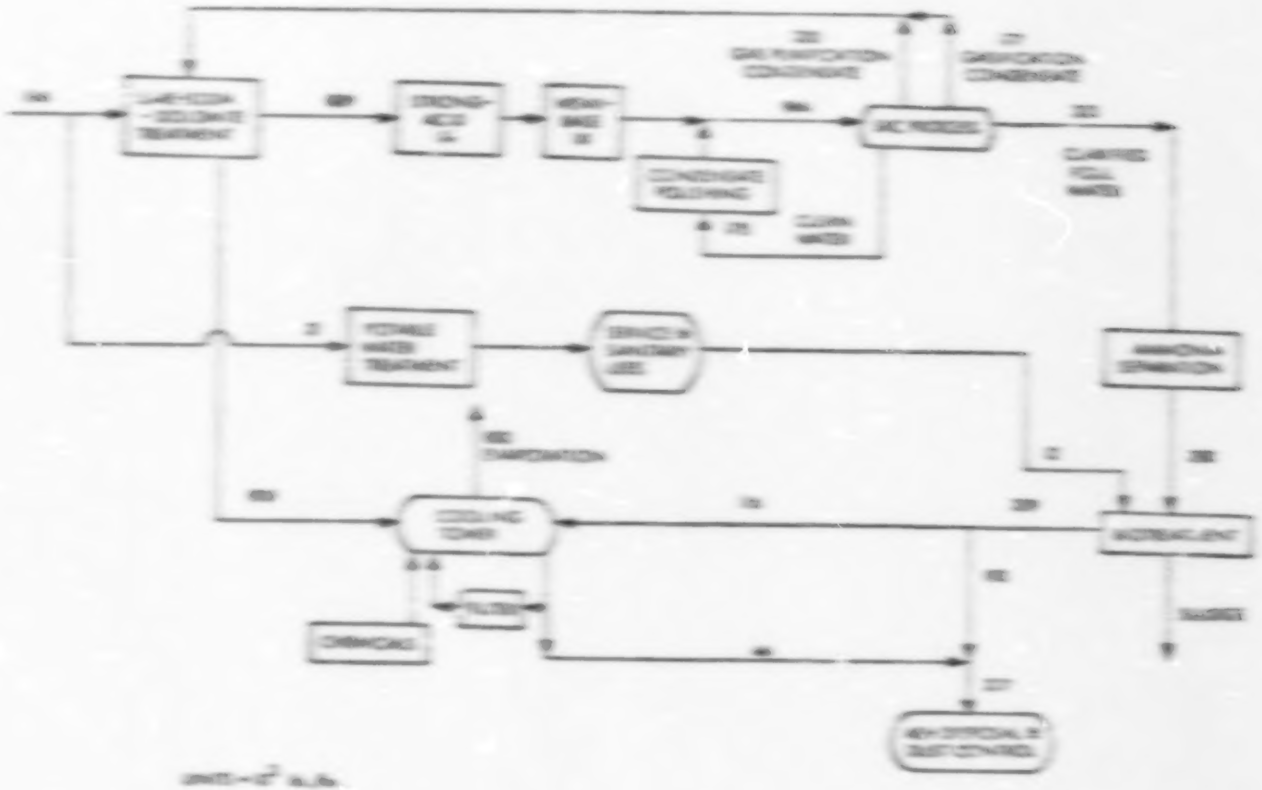
The residue from reverse osmosis contains 3.6 percent soluble salt (mostly $CaCl_2$). The disposal of this residue has not been studied and no added cost has been assumed. In New Mexico, where the source water is brackish and the major positive ion is Na^+, segregation and separate disposal of soluble waste has been assumed required for all plants and lined evaporation ponds have been costed.

Solvent Refined Coal

The SRC process is a net producer of water, but it takes in water of a quality suitable for low pressure boilers and puts out four streams: 323×10^3 lb/hr foul condensate, 120×10^3 lb/hr water (after flashing) from gas purification having the approximate composition of Table 14-13, 177×10^3 lb/hr condensate from the Koppers-Totzek gasifiers having the approximate composition of Table 14-12, and 175×10^3 lb/hr clean water (after flashing) from the reformers which can be returned to the boilers with other condensate. In addition the plant takes in raw water of the composition given on Table 14-1. Various ways have been considered to combine these streams for use in the cooling tower and in the boiler. The most satisfactory and flexible is to blend the two intermediate quality effluent streams with raw water and treat the blend to approaching boiler feed quality using the same quality for cooling tower makeup. This is shown in Figure 19-6. This procedure results in a low cooling tower blowdown with savings in chemicals and a large and economical lime clarifier.

The approximate blended water composition is shown on Table 19-8 with the approximate composition of the water leaving the lime-soda treatment. Lime, soda ash and additional magnesium as dolomite are needed for the chemical treatment. The approximate rates are lime 290 lb/hr, soda ash 220 lb/hr and dolomite 550 lb/hr. Chemical costs are given on Table 15-3 and result in a total cost of $20/hr. The clarifiers will cost about $560,000 or $12/hr.

The cooling tower will require a large side stream filter to hold suspended solids to 300 mg/l because all the makeup (from all sources) is overflow from clarifiers and not clear. A side stream of about 1,000 gal/min is probably required, so the filters cost about $5/hr including flocculating chemicals. The cooling tower is limited to 20 cycles of concentration by chloride (because of the high chloride content of the foul condensate) or


LIME-SODA-ZEOLITE TREATMENT
STRONG-ACID IX
WEAK-BASE IX
CONDENSATE POLISHING
CLEAN WATER
SRC PROCESS
GASIFICATION CONDENSATE
CONDENSATE
CLARIFIED FOUL WATER
POTABLE WATER TREATMENT
SERVICE & SANITARY USES
AMMONIA SEPARATION
EVAPORATION
COOLING TOWER
BIOTREATMENT
FILTER
CHEMICALS
ASH DISPOSAL & DUST CONTROL

units—10^3 lb/h

Figure 19-4. Water treatment plant block diagram for SRC at North Dakota.

TABLE 19-8. APPROXIMATE INFLUENT TO AND EFFLUENT FROM LIME-SODA-SILICA TREATMENT IN SRC PLANT AT NORTH DAKOTA

	Influent (mg/l)	Effluent (mg/l)
Ca	55	12
Mg	26	2.5
HCO_3	125	0
SO_4	130	130
Cl	19	19
SiO_2	≈ 10	≈ 1
PO_4	6	0
NH_3	13	13
COD	7	7

25 cycles of concentration by calcium sulfate. The difference is unimportant. Biocide, anticorrosion chemicals and suspending agents cost about $10/hr.

The boiler treatment costs about $1.8 × 10^6/yr, including resin replacement and chemicals: about $50/hr.

The cost of ammonia separation, taken from Figure 16-4, for 0.93 × 10^6 gallons/day is $4.6/thousand gallons = $178/hr. There being about 12,000 mg/l in the foul condensate, about $256/hr is recovered from the sale of ammonia. The energy required is 66 × 10^6 Btu/hr.

Biotreatment costs $0.021/lb BOD removed and about 30,000 mg/l BOD are removed. The cost is $189/hr. The energy requirement is 18 × 10^6 Btu/hr as steam plus 1670 kw. These numbers are summed up below.

	$/hr	10^6 Btu/hr	kw
Boiler feed treatment	50	--	--
Lime soda softener and chemicals	40	--	--
Cooling water filter and chemicals	15	--	--
Ammonia separation	(+78)	66	--
Biotreatment	189	18	1670

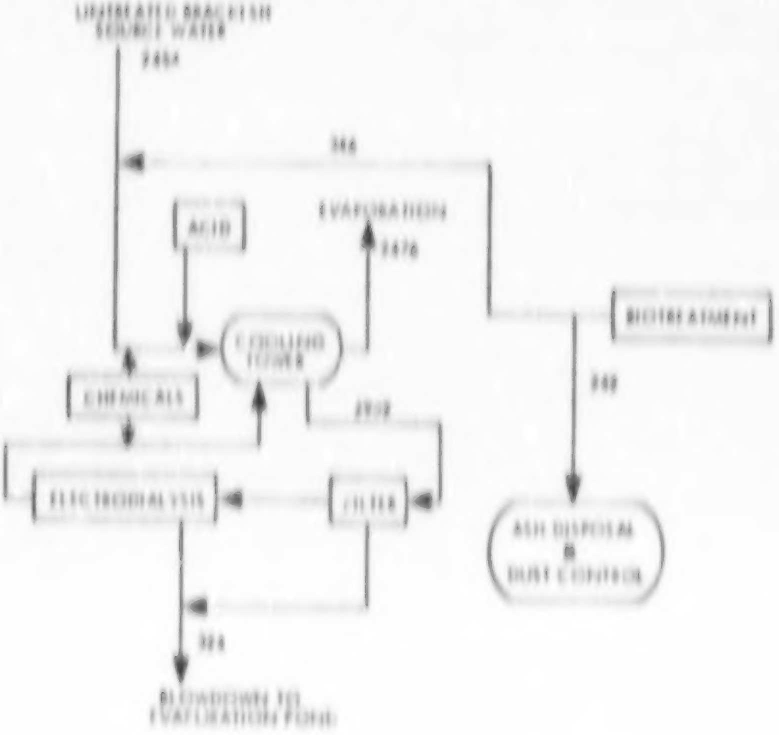
19.3 PLANTS IN NEW MEXICO

Power Plant

The overriding problem in all the exemplary plants sited in New Mexico is that the source water is assumed to be brackish and to have the composition shown on Table 14-2. Desalting procedures are required for all water uses. For the boiler feed water desalting is needed to save excessive use and cost of ion exchange demineralizers. Desalting is needed to make the water fit for revegetation and drinking use. In the cooling towers the decision has been made that the salt in the source water may not be disposed of with the ash but must be segregated and separately disposed of in a lined evaporation pond. This means either that the makeup to the cooling tower must be desalted or that the blowdown must be segregated.

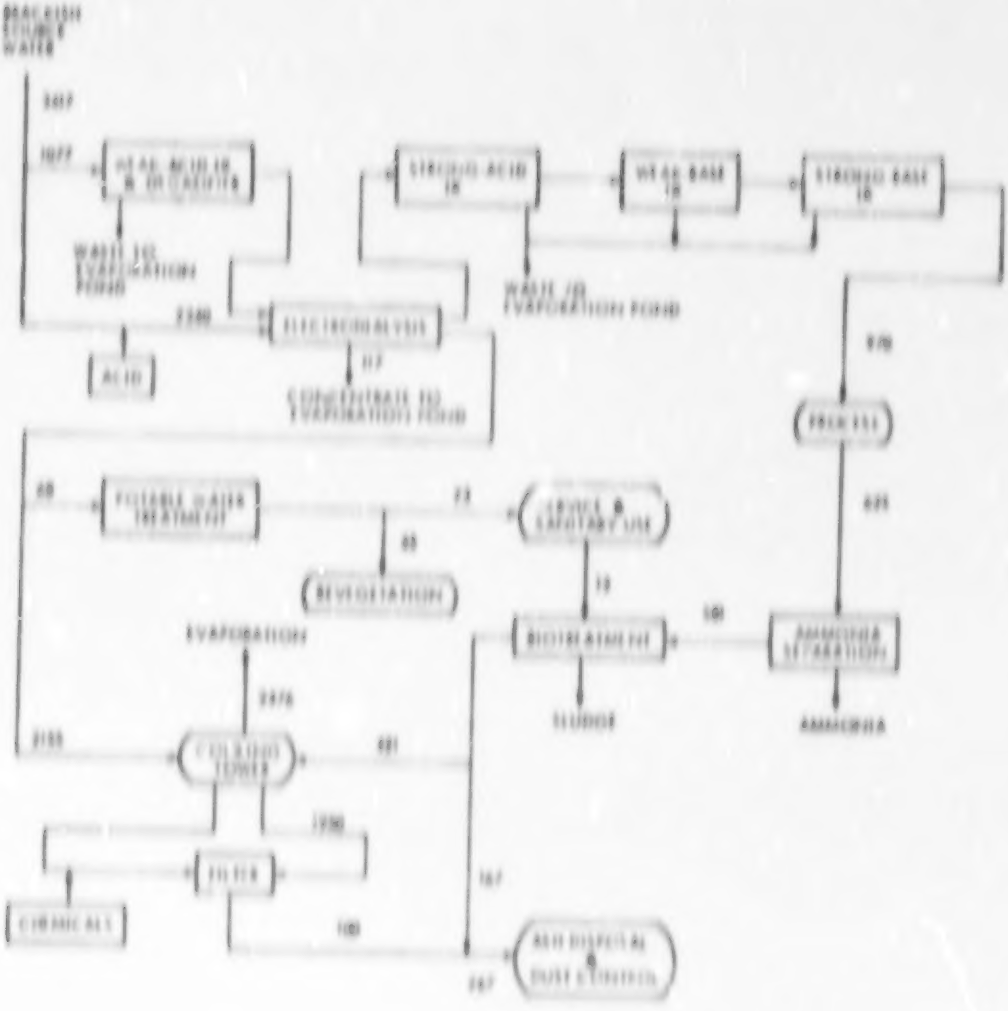
If raw source water is used as makeup to the cooling tower mixed with effluent from biotreatment, it must be acidified to remove bicarbonate. The next limit is excessive chloride in the circulating water which occurs at 4 cycles of concentration. A side stream must be taken from the tower and treated, first to remove suspended solids which interfere with the desalting procedure and then to concentrate and reject the dissolved solids. The reject will be saturated in calcium sulfate which is as concentrated as the reject can be without precipitation occurring. Precipitation is not permissible in either electrodialysis or reverse osmosis desalting procedures. This possible scheme is shown in Figure 19-7. A side stream electrodialysis system as shown is a device essentially to concentrate salt for removal, not a device to produce desalted water. The concentrations in and out are not the same and the cost figures given in Section 15 do not necessarily apply. Electrodialysis for salt concentration is available from Dow Chemical, who made a cost estimate for this report. The overall plant cost for the systems shown on Figure 19-7, with side stream desalting, and Figure 19-8, with makeup desalting, are close to the same. We are investigating side stream desalting further but for this study, because we are unsure of the basis of the cost estimate, the scheme of Figure 19-8 is the one used.

For simple removal of ionic species at the throughput of this plant,


UNTREATED BRACKISH SOURCE WATER
2454
366
ACID
EVAPORATION
2476
BIOTREATMENT
COOLING TOWER
CHEMICALS
2912
242
ELECTRODIALYSIS
FILTER
ASH DISPOSAL & DUST CONTROL
324
BLOWDOWN TO EVAPORATION POND

UNITS = 10^3 lb./hr.

Figure 19-7. Use of untreated brackish makeup to cooling tower of power plant at New Mexico.


BRACKISH SALINE WATER
ELECTRODIALYSIS
ACID
STRONG ACID IX
WEAK BASE IX
STRONG BASE IX
WASTE TO EVAPORATION POND
CONCENTRATE TO EVAPORATION POND
PROCESS
POTABLE WATER TREATMENT
SERVICE & SANITARY USE
REVEGETATION
EVAPORATION
BIOTREATMENT
AMMONIA SEPARATION
SLUDGE
AMMONIA
COOLING TOWER
FILTER
CHEMICALS
ASH DISPOSAL & DUST CONTROL
1077
117
2376
2155
167
100
267

Unit : 10^3 lb/hr.

Figure 19-8. Water treatment plant block diagram for electric generation at New Mexico.

electrodialysis uses more energy than reverse osmosis, but the total operating cost is lower. Electrodialysis does not remove any non-ionic species, while reverse osmosis does partly remove such molecules. In particular, reverse osmosis partly removes silica. As it turns out, silica is not a limitation in the operation of the cooling tower and electrodialysis has been selected for desalting.

A three-stage electrodialysis system will reduce the total dissolved ionic content to about 1/8th (see section 15.6 for costs). Because the electrodialysis plant will separately handle the boiler feed water and because so much of the capital cost of electrodialysis is in rectifying equipment, economy of scale is realized and the capital cost is based on a throughput of $3,400 \times 10^3$ lb/hr = 10^7 gallons/day. From Figure 15-5 the capital cost is $0.32/(gallons/day). For that part of the flow used for cooling water makeup and revegetation, = $2,200 \times 10^3$ lb/hr = 6.3×10^6 gallons/day, the cost and energy requirement of electrodialysis can now be estimated. Capital charges at 17%/yr for 8,000 hrs/yr of $0.32 \times 6.3 \times 10^6$ dollars investment = $42.8/hr. Membranes, filters and chemicals at $0.2/thousand gallons cost $52.5/hr. Electricity at 0.4 kw-hr/(thousand gallons)(100 mg/l removed) and $0.02/kw-hr costs $48.9/hr. Acid costs $2.9/hr. The total cost is $147/hr and the total energy is 2560 kw.

The cooling tower requires a side stream filter to remove suspended solids from the air and from the effluent of the biotreatment. The filter will handle about $1,950 \times 10^3$ lb/hr of side stream flow and costs about $12/hr including flocculating chemicals. Biocide and anticorrosion chemicals, considering the large amount of effluent from biotreatment used as cooling tower makeup, cost about $18/hr.

The boiler feed water is first treated with a weak acid ion exchange resin to remove Ca^{++}, Mg^{++} and some Na^+ and replace these ions with H^+. The hydrogen ion combines with HCO_3^- and $CO_3^=$ to yield CO_2 which is released in a degasifier. H_2SO_4 is used to regenerate the resin at 110 percent of stoichiometric to the $HCO_3^- + CO_3^=$. Removal of the alkalinity is necessary to prevent precipitation in the electrodialysis equipment. However, sulfate must also be removed downstream so weak acid exchange is used in preference to direct acid addition.

The water then passes through a three-stage electrodialysis unit to reduce the total dissolved solids to about 1/8th through a strong acid ion exchange and a weak base ion exchange to further remove Na^+ and $SO_4^=$; and through a strong base ion exchange to remove silica. The composition of the boiler feed at various points in the treatment is shown on Table 19-5.

The cost of operating the electrodialysis unit for 1340×10^3 lb/hr = 3.8×10^6 gallons/day is $89/hr and the electric usage is 1300 kw.

The ion exchange system cost is 3.4×10^6 dollars (quotation from Permutit) or $69/hr, including resin replacement. Regeneration chemical requirements are: H_2SO_4, 660 lb/hr and NaOH, 200 lb/hr for a cost of $43/hr. The total ion exchange system cost is $112/hr.

A return condensate polishing system will be required; the cost is small.

The foul condensate treatment was costed using the procedures described in Sections 16 and 18 and used in Section 19.2.

The electrodialysis concentrate and the ion exchange regeneration waste amount to about 275×10^3 lb/hr and are sent to a lined evaporation pond. At this site the net annual average evaporation rate after rainfall is 53 inch/yr = 33 gallons/(ft^2)(yr). For sizing the pond an allowance of

TABLE 19-5. COMPOSITIONS AT POINTS IN THE BOILER FEED WATER TREATMENT IN NEW MEXICO

	Entering Electrodialysis (mg/l)	Leaving Electrodialysis (mg/l)	After Weak Base Resin (mg/l)	After Strong Base Resin (mg/l)
Ca^{++}	0	0	0	0
Mg^{++}	0	0	0	0
Na^+	743	93	3	3
$CO_3^=$	0	0	0	0
HCO_3^-	0	0	0	0
SO_4	509	63	1	1
Cl	770	93	1	1
SiO_2	6	6	6	< 1

30 percent was made and 26 gallons/(ft^2)(yr) = 0.027 lb/(ft^2)(hr) was used. The pond is 10.2 × 10^6 ft^2 (234 acres) which, at 20¢/ft^2, costs $2.04 × 10^6. This is amortized at 15%/yr or $35/hr.

The total plant costs and energy requirements are:

	$/hr	10^6 Btu/hr	kw
Ion Exchange	112	--	--
Electrodialysis	236	--	1760
Cooling tower filter and chemicals	30	--	--
Ammonia Separation	139*	129	--
Biotreatment	219	21	1000
Evaporation Pond	35	--	--

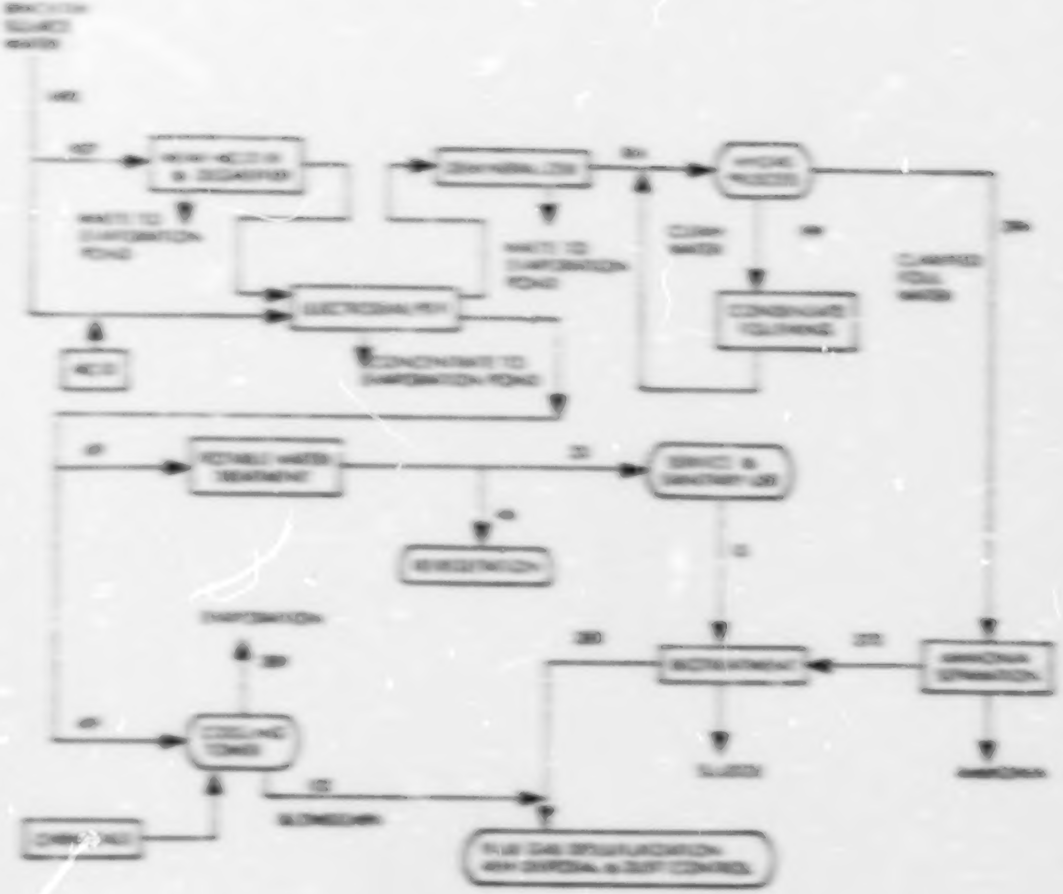
---

*After recovering $165/hr from the sale of ammonia.

Hygas

The water treatment block diagram is quite similar to that for the power plant and is shown on Figure 19-9. The cycles of concentration in the cooling tower are low enough that no side stream treatment is required. In this plant, where the biotreated effluent is used only for disposal with solids, as high a level of treatment as high purity oxygen may not be necessary and less expensive alternatives should be considered. The boiler makeup must meet high pressure specifications, and the block marked "demineralizer" is like the blocks shown on Figure 19-8 but contains a mixed bed ion exchange as well.

The cost and energy requirements are:


BRACKISH SOURCE WATER
ION EXCHANGE & DEGASIFIER
WASTE TO EVAPORATION POND
DEMINERALIZER
WASTE TO EVAPORATION POND
HYGAS PROCESS
CLEAN WATER
CONDENSATE POLISHING
CLARIFIED FOUL WATER
ELECTRODIALYSIS
ACID
CONCENTRATE TO EVAPORATION POND
POTABLE WATER TREATMENT
SERVICE & SANITARY USE
REVEGETATION
EVAPORATION
COOLING TOWER
BLOWDOWN
CHEMICALS
BIOTREATMENT
AMMONIA SEPARATION
SLUDGE
AMMONIA
FLUE GAS DESULFURIZATION ASH DISPOSAL & DUST CONTROL

UNITS—m^3/h

Figure 19-4. Water treatment plant block diagram for Hygas process at New Mexico.

	$/hr	10^6 Btu/hr	kw
Ion Exchange	34	--	--
Electrodialysis	103	--	1650
Ammonia separation	6*	60	--
Biotreatment	89	7	640
Cooling water chemicals	19	--	--
Evaporation Pond	21	--	--

*After recovering $78/hr from the sale of ammonia.

HRC

This water treatment block diagram is also similar to that for the power plant and is shown on Figure 19-10. The cycles of concentration in the cooling tower are about 7, low enough that only a dust filter is required in the side stream to remove the suspended solids. The cost and energy requirements are:

	$/hr	10^6 Btu/hr	kw
Ion Exchange	40	--	--
Electrodialysis	45	--	740
Ammonia separation	(49 INCOME)*	44	--
Biotreatment	126	12	1080
Cooling water filter and chemicals	11	--	--
Evaporation Pond	9	--	--

*After recovering $170/hr from the sale of ammonia.

19.4 PLANTS IN WYOMING

Electric Generation

At all plants in Wyoming, sewage from a satellite town is assumed to be

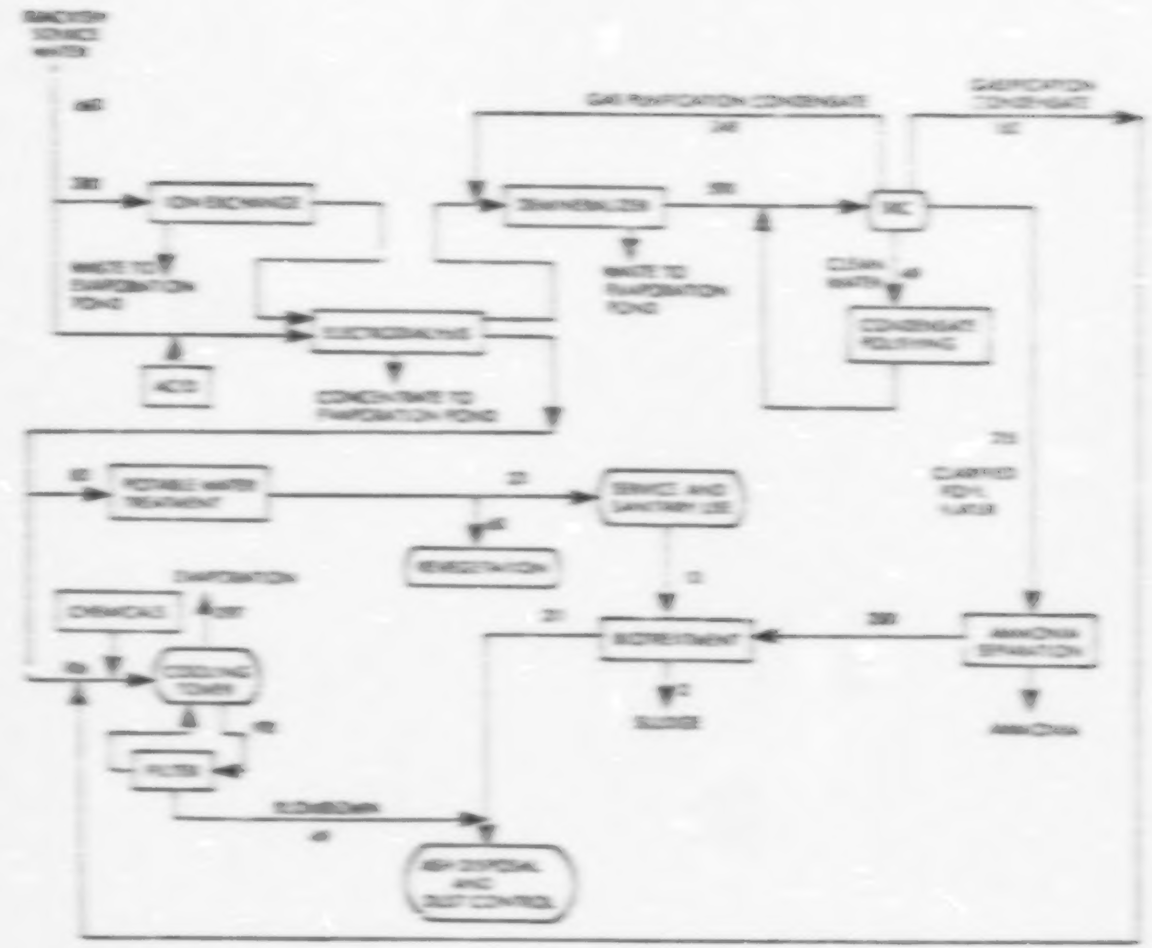

BRACKISH SERVICE WATER
ION EXCHANGE
WASTE TO EVAPORATION POND
ELECTRODIALYSIS
ACID
CONCENTRATE TO EVAPORATION POND
GAS PURIFICATION CONDENSATE
GASIFICATION CONDENSATE
DEMINERALIZER
WASTE TO EVAPORATION POND
SRC
CLEAN WATER
CONDENSATE POLISHING
CLARIFIED FOUL WATER
POTABLE WATER TREATMENT
SERVICE AND SANITARY USE
REVEGETATION
EVAPORATION
CHEMICALS
COOLING TOWER
FILTER
BLOWDOWN
ASH DISPOSAL AND DUST CONTROL
BIOTREATMENT
SLUDGE
AMMONIA SEPARATION
AMMONIA

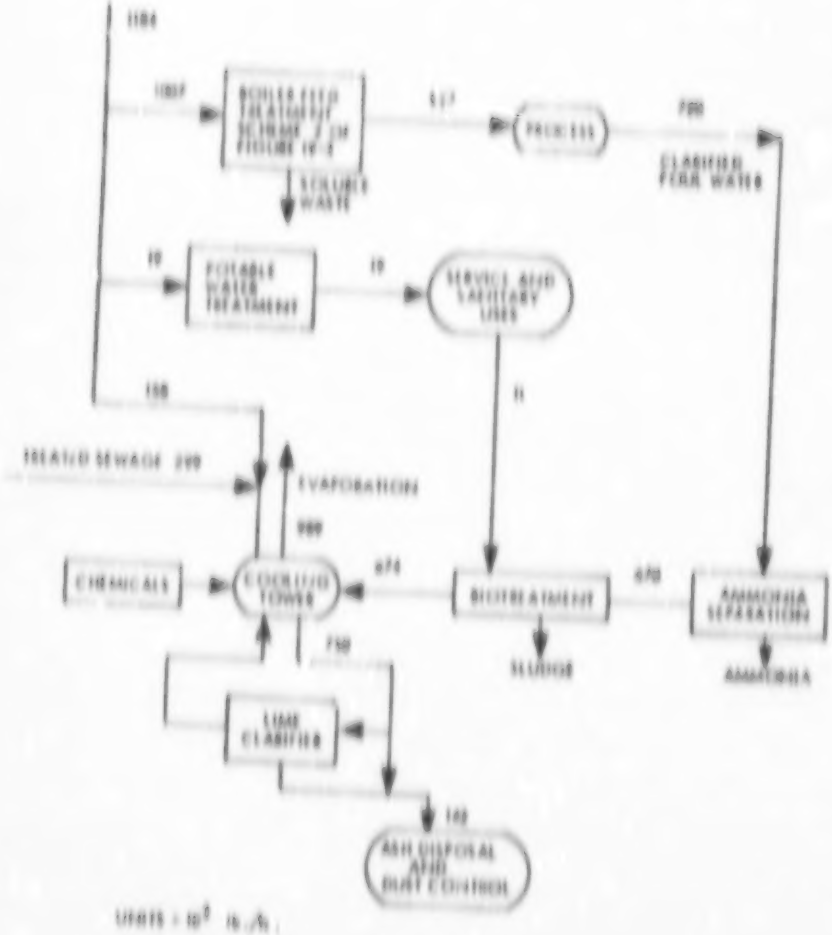
Figure 23-22. Water treatment plant block diagram for SRC at New Mexico.

taken into the plant and treated in a small package-type treatment facility, the effluent from which has the composition of Table 14-3. Additional water, having the composition shown on Table 14-4 which is the best quality of any of the sites, is available but is very expensive. The power plant at this site uses partial dry cooling for the turbine condensers, but the cooling water requirement is still so large that fresh water is needed. The boiler is fed with treated fresh water; the treatment is no different from that described for plants in North Dakota, shown as Scheme 2 of Figure 19-3.

The scheme for this plant is shown in Figure 19-11. The blended cooling water has the approximate composition of Table 19-10. Because the evaporation rate is lower than at other power plants, the cooling tower is required to work only at about eight cycles of concentration. At eight cycles chloride will reach 3,200 mg/l, which is just tolerable. The other limitations are phosphate and bicarbonate, which must be removed. Also, the makeup has high suspended solids. A combined lime treatment clarifier is required. This treatment can be placed in a side stream, in which case a side stream rate of about 750 × 10^3 lb/hr suffices to hold phosphate below 24 mg/l, bicarbonate below 188 mg/l and suspended solids below 300 mg/l. Alternatively, the two biotreatment effluent waters can be lime treated and clarified before going to the tower makeup. This involves a flow rate of about 930 × 10^3 lb/hr and keeps phosphate and bicarbonate very low. Dust drawn in from the air may raise the suspended solids concentration in the circulating water undesirably

TABLE 19-10. COOLING WATER MAKEUP TO THE ELECTRIC POWER PLANT IN WYOMING

	mg/l		mg/l
Ca	34	SS	100
Mg	18	COD	> 200
HCO_3	133	NH_3	20
SO_4	50		
Cl	396		
SiO_2	12		
PO_4	17		


BOILER FEED TREATMENT SCHEME 2 IN FIGURE 19-2
PROCESS
SOLUBLE WASTE
CLARIFIED FOUL WATER
POTABLE WATER TREATMENT
SERVICE AND SANITARY USES
TREATED SEWAGE
EVAPORATION
CHEMICALS
COOLING TOWER
BIOTREATMENT
AMMONIA SEPARATION
SLUDGE
AMMONIA
LIME CLARIFIER
ASH DISPOSAL AND DUST CONTROL

UNITS: 10^3 lb./h.

Figure 19-11. Water treatment plant block diagram for electric generation at Wyoming.

high. Side stream, rather than makeup, treatment seems preferable, but the cost is independent of the location.

The cooling water makeup has a high nitrogen, phosphorus and carbon content. This may be the most nutrient water used at any site. The cost of biocides will be high; $1.50/thousand gallons of blowdown has been assumed.

Other treatments are as previously used at other sites. The cost and energy requirements are:

	$/hr	10^6 Btu/hr	kw
Ion exchange for boiler feed	90	--	--
Cooling tower clarifier and chemicals	55	--	--
Ammonia separation	160*	147	--
Biotreatment	251	23	2170

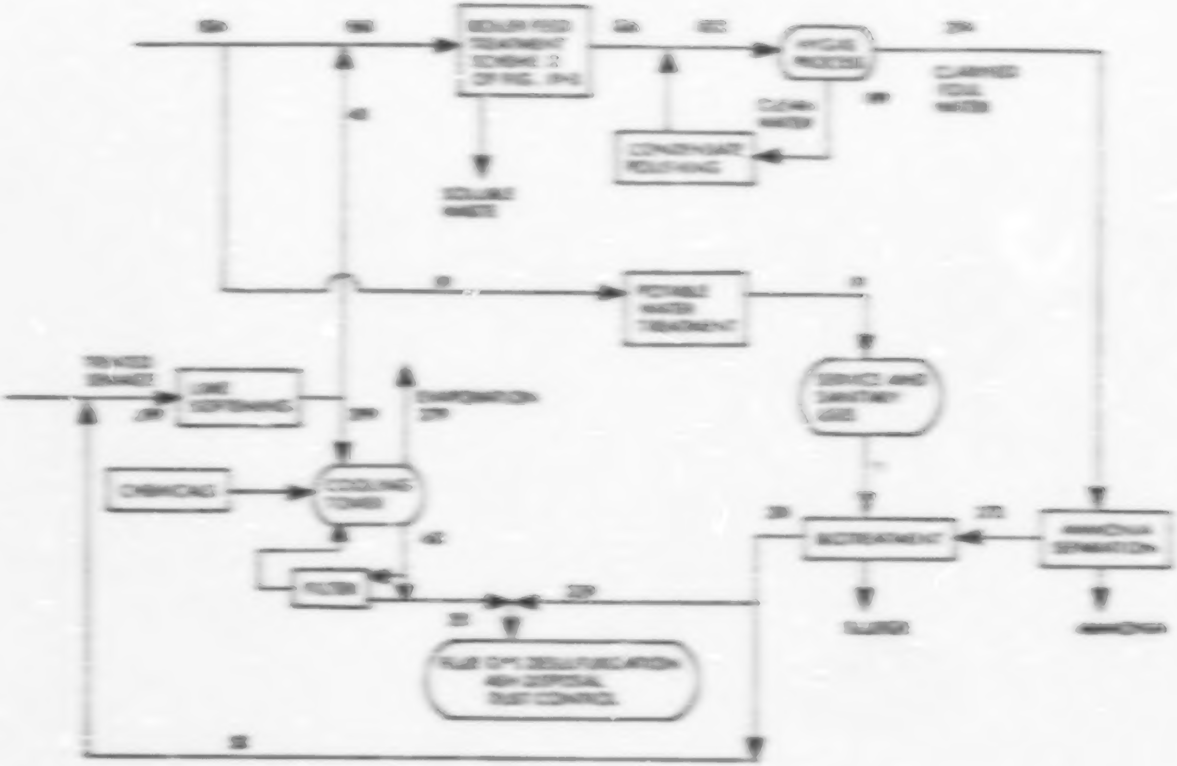
---

*After recovering $100/hr from sale of ammonia.

Hygas

In this plant the sewage water plus the treated process effluent total close to the whole cooling water makeup requirement. Fresh water is used for boiler feed. In operating the cooling system the same choice is available as for the Hygas plant in North Dakota, namely to operate at low cycles of concentration, to blowdown onto the ash and to pay heavily for biocide and other chemicals, or to operate at high cycles of concentration, to treat the makeup and to avoid wasting chemicals. The latter scheme has been used as in North Dakota. As found in Reference 2, treated sewage can be concentrated by 15 cycles without problem and this is what will be done. The scheme is shown on Figure 19-12.

The cost and energy requirements are:


BOILER FEED TREATMENT SCHEME 2 OF FIG. 19-6
HYGAS PROCESS
CLARIFIED FOUL WATER
CLEAN WATER
CONDENSATE POLISHING
SOLID WASTE
POTABLE WATER TREATMENT
TREATED SEWAGE
LIME SOFTENING
EVAPORATION
CHEMICALS
COOLING TOWER
FILTER
SERVICE AND SANITARY USE
BIOTREATMENT
AMMONIA SEPARATION
SLUDGE
AMMONIA
FLUE GAS DESULFURIZATION ASH DISPOSAL DUST CONTROL

UNITS-10^6 g/h

Figure 19-11. Water treatment plant block diagram for Hygas process at Wyoming.

	$/hr	10^6 Btu/hr	kW
Ion exchange for boiler feed	94	--	--
Cooling water treatment and chemicals	31	--	--
Ammonia separation	77*	60	--
Biotreatment	89	7	665

*After recovering $77/hr from the sale of ammonia.

Synthane

The Synthane process takes in more boiler feed water and puts out more dirty water than the Hygas process. Also, 158×10^3 lb/hr of intermediate quality water is obtained from the process. The composition of this water is not known, but it is assumed to have one tenth the concentration of the foul condensate. If this intermediate quality water were to be treated with the sewage, it would have to be stripped of ammonia. It is best, therefore, to treat this water with foul condensate where the ammonia can be consumed and it will not be necessary to pass it through ammonia separation. Since foul condensate is stripped of ammonia, this can be done to a slightly lower concentration with little increase in cost. This saves the expense of stripping the intermediate quality water.

The effluent from the biotreatment of foul condensate is assumed to have 600 mg/l chloride and, even when diluted with treated sewage, this is too much chloride for cooling water makeup. The scheme shown in Figure 19-13, which is similar to the Hygas scheme, will not work. Since desalting is required and since some effluent from one of the biotreatments will go to boiler feed, we will use the desalted water for boiler feed; that is, the scheme of Figure 19-14 will be used.

The cooling water and lime softening on Figure 19-14 is the same as was used in the Hygas plant at Wyoming shown on Figure 19-12. The reverse osmosis is a smaller version of the equipment used on the power plant in North Dakota. However, in the power plant in North Dakota we did not feed the effluent from reverse osmosis to a boiler, and here we will. The approximate

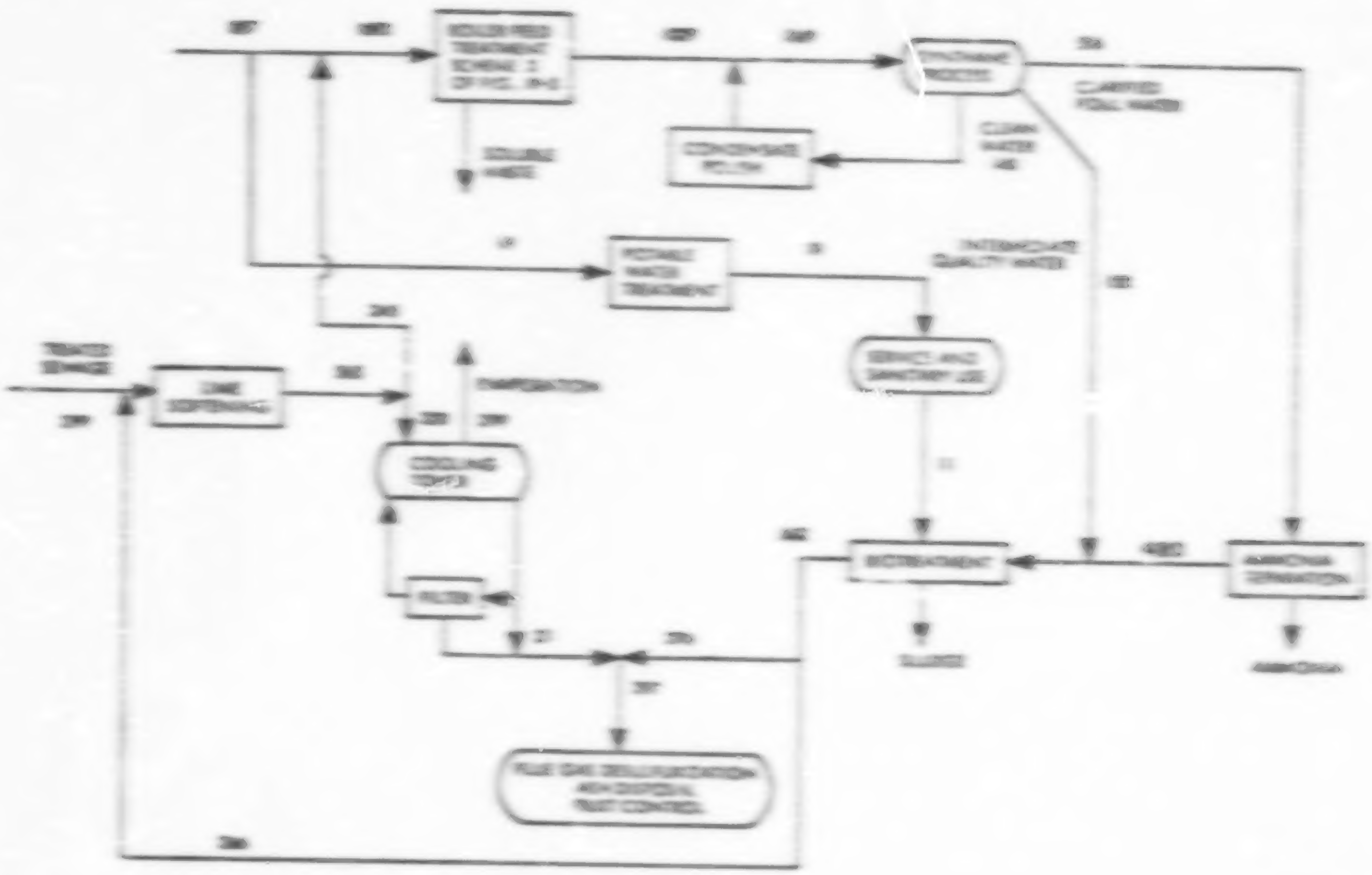
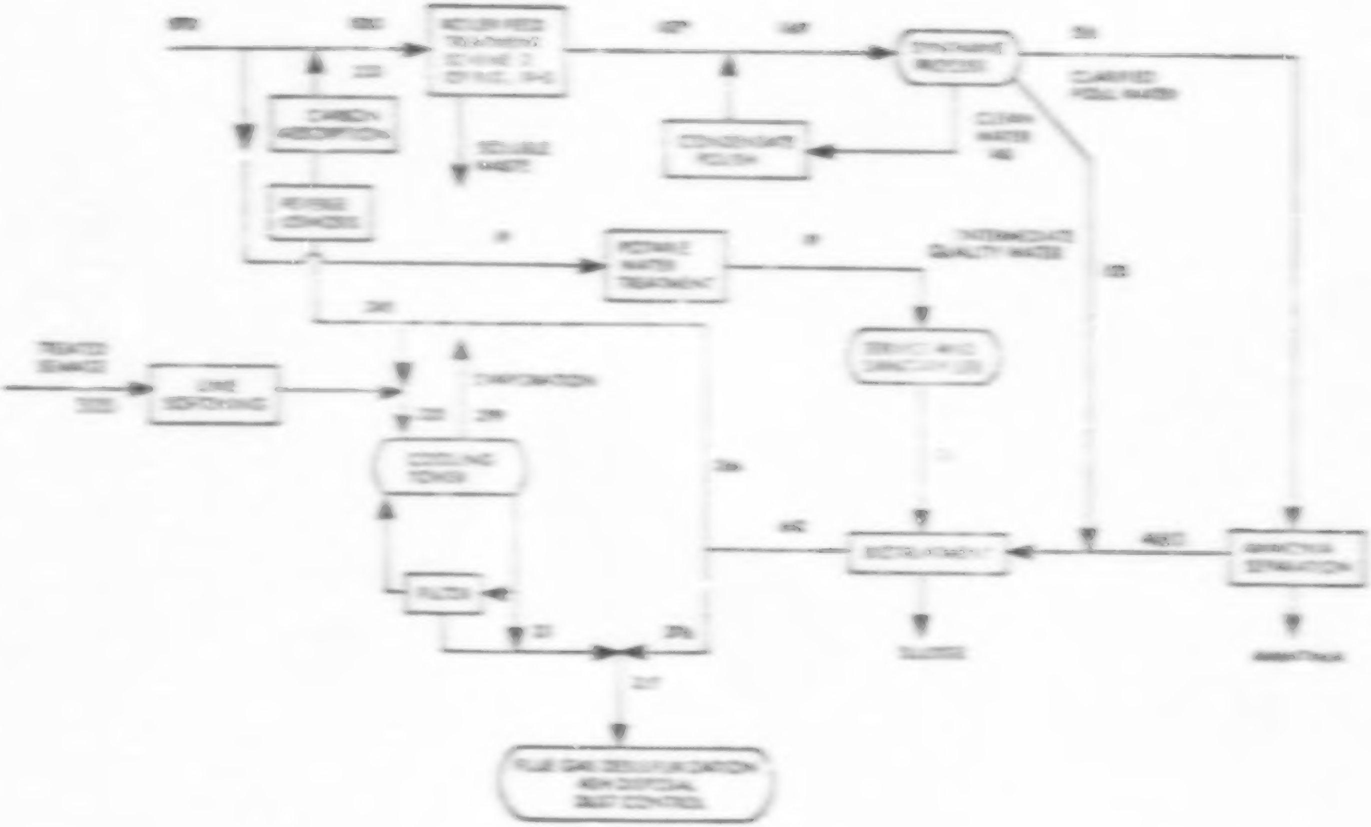

BOILER FEED TREATMENT SCHEME 1
BOILER WASTE
CONDENSATE POLISH
SYNTHANE PROCESS
CLARIFIED FOUL WATER
CLEAN WATER
POTABLE WATER TREATMENT
INTERMEDIATE QUALITY WATER
TREATED SEWAGE
LIME SOFTENING
EVAPORATION
SERVICE AND SANITARY USE
COOLING TOWER
FILTER
BIOTREATMENT
AMMONIA SEPARATION
SLUDGE
AMMONIA
FLUE GAS DESULFURIZATION ASH DISPOSAL DUST CONTROL

Figure 15-11. Water treatment plant block diagram for Synthane process at Wyoming (Scheme 1, not used).


BOILER FEED TREATMENT SCHEME 2
CARBON ADSORPTION
POTABLE USAGES
SOLIDS WASTE
CONDENSATE POLISH
SYNTHANE PROCESS
CLARIFIED FOUL WATER
CLEAN WATER
POTABLE WATER TREATMENT
INTERMEDIATE QUALITY WATER
SERVICE AND SANITARY USE
TREATED SEWAGE
LIME SOFTENING
EVAPORATION
COOLING TOWER
FILTER
BIOTREATMENT
AMMONIA SEPARATION
SLUDGE
AMMONIA
FLUE GAS DESULFURIZATION ASH DISPOSAL DUST CONTROL

UNITS—10^3 lb/hr.

Figure 19-24. Water treatment plant block diagram for Synthane process at Wyoming (Scheme 2, as used).

composition is given in Section 19.2. However, COD or organic matter is not shown in Section 19.2 and is not known. It has been arbitrarily assumed that 1,000 mg/l is to be removed by carbon adsorption at a cost of $1.5/thousand gallons, or $42/hr (see Figure 15-1), and an energy requirement of about 11,000 Btu/lb COD removed, or 2.6×10^6 Btu/hr.

The costs and energy requirements can now be tabulated:

	$/hr	10^6 Btu/hr	kw
Ion exchange for boiler feed	118	--	--
Cooling water treatment and chemicals	31	--	--
Ammonia separation	115*	105	--
Biotreatment	212	28	2680
Reverse osmosis	46	--	210
Carbon adsorption	42	3	--

---

*After recovering $136/hr from sale of ammonia.

Solvent Refined Coal

Being given the sewage from the satellite town, this plant has a very small net consumption of additional water. However, there are four different water streams required and five different water streams available. Before making economic studies some reasonable schemes must be devised. The four required water streams, taking approximate account of losses in treatment, are:

Feed to ion exchange for boiler after returning clean process water	662×10^3 lb/hr
Drinking water	19×10^3 lb/hr
Evaporated in cooling tower	229×10^3 lb/hr
For ash disposal and dust control	178×10^3 lb/hr
Total	1088×10^3 lb/hr

The five available water streams, again taking approximate account of losses in treatment, are:

Fresh water	98×10^3 lb/hr
Water from gas purification	261×10^3 lb/hr
Water from gasifiers	163×10^3 lb/hr
Treated sewage from satellite town plus plant complex	310×10^3 lb/hr
Partially-treated foul condensate	256×10^3 lb/hr
Total:	1088×10^3 lb/hr

The next step is to record which available water streams are good for which requirements without treatment:

Fresh water and water from gas purification are good for all uses.
Water from gasifiers and treated sewage are good only for ash disposal and dust control.
Foul condensate is good for nothing.

Minimum water treatment will be required if the preliminary and incomplete scheme of Figure 19-15 is used. Broadly speaking, either sewage or foul condensate has too high a chloride content (600 mg/l) to go to a cooling tower without desalting, whereas sewage can be treated and used as cooling tower makeup without removal of chloride. For boiler feed desalting is required anyway, so foul condensate will be used. This leads to the scheme of Figure 19-16, which is based in part on work reported in Reference 3 and described in Section 15.5.

The cost and energy requirements can now be summed up and then briefly derived.

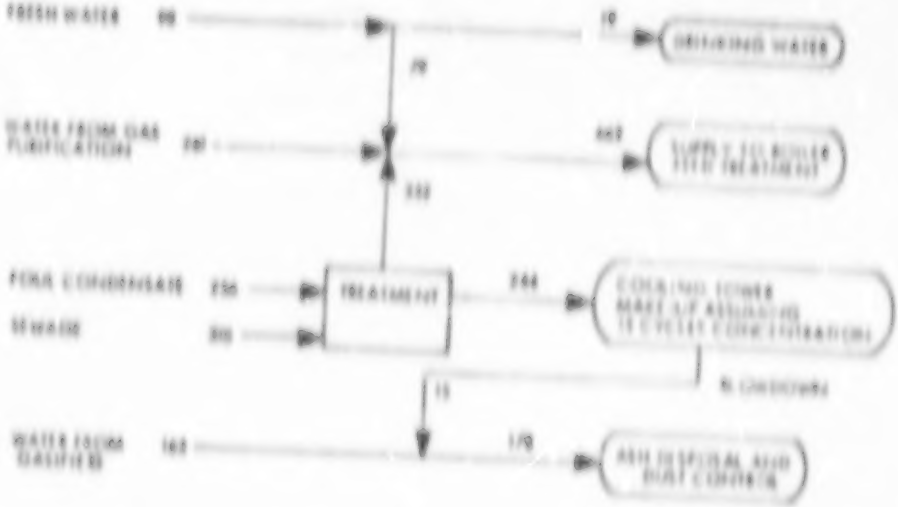

FRESH WATER
DRINKING WATER
WATER FROM GAS PURIFICATION
SUPPLY TO BOILER FEED TREATMENT
TREATMENT
SEWAGE
COOLING TOWER MAKE-UP ASSUMING (3 CYCLES CONCENTRATION)
BLOWDOWN
WATER FROM GASIFIER
ASH DISPOSAL AND DUST CONTROL

Figure 19-15. Preliminary water treatment plant block diagram for Solvent Refined Coal at Wyoming.

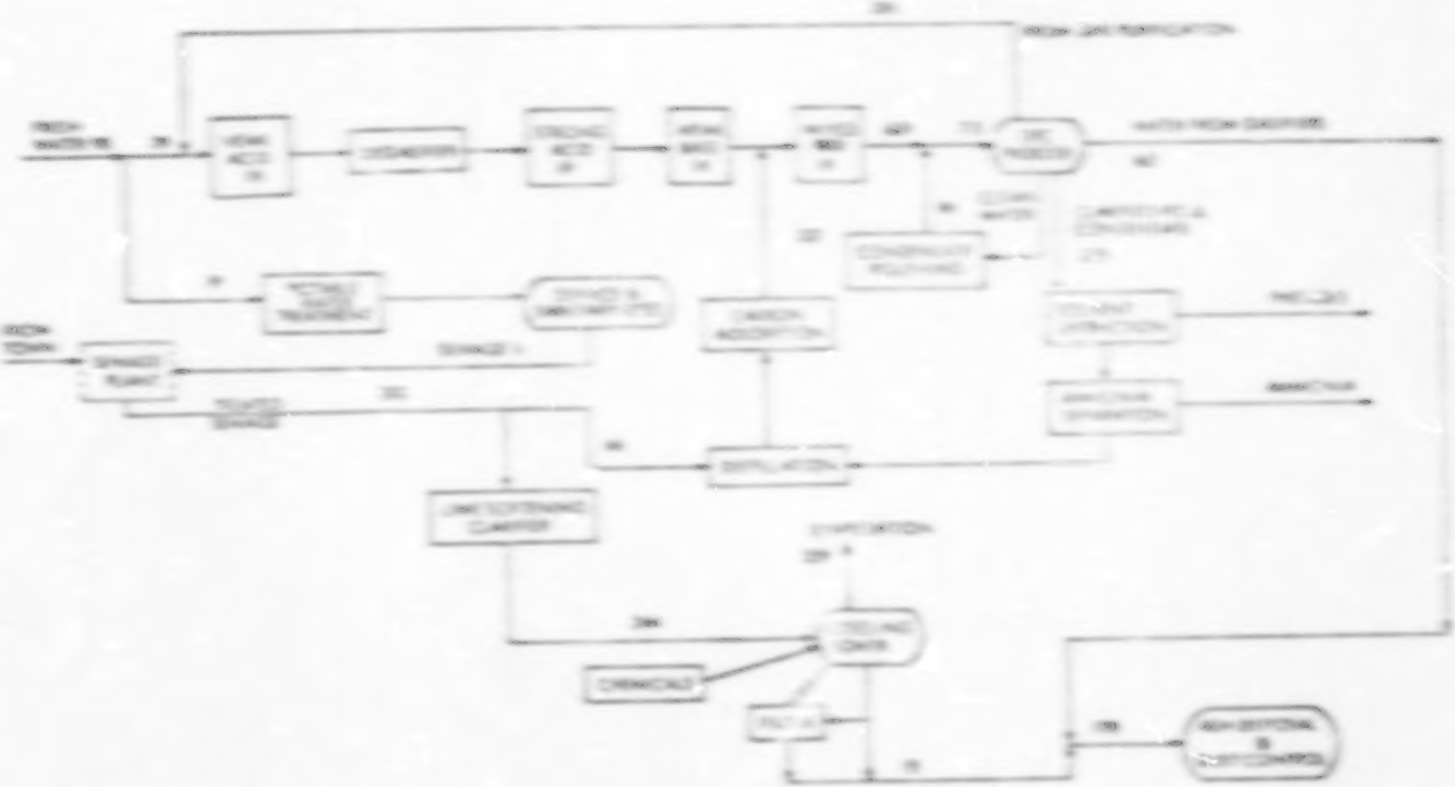

FRESH WATER IN
DEGASIFIER
IGC PROCESS
FROM GAS PURIFICATION
CONDENSATE POLISHING
POTABLE WATER TREATMENT
CARBON ADSORPTION
SOLVENT EXTRACTION
AMMONIA SEPARATION
AMMONIA
SEWAGE PLANT
FROM TOWN
TREATED SEWAGE
DISTILLATION
LIME SOFTENING CLARIFIER
EVAPORATION
COOLING TOWER
CHEMICALS
FILTER
ASH DISPOSAL & DUST CONTROL

Figure 19-16. Water treatment plant block diagram for IGC at Wyoming.

	$/hr	10^6 Btu/hr	kw
Ion exchange	48	--	--
Cooling water treatment and chemicals	28	--	--
Solvent extraction	147	33	--
Ammonia separation	(63 INCOME)	56	--
Distillation	132	35	--
Carbon adsorption	10	0.3	--

The ion exchange system for demineralizing boiler feed is similar to others used. The mixed bed, which is assumed to handle the full flow including distilled water, has been added as a protection because the quality of the distilled water is not well defined. It may not be necessary for the low pressure boiler of this plant. In any event the chemical requirements are very small for this bed. The chemical requirements are measured by a flow of only 140 × 10^3 lb/hr and are about $10/hr. The capital cost is about $2.0 × 10^6, or $38/hr.

The cooling tower treatment is just a little smaller than in the Hygas and Synthane plants.

For solvent extraction, approximate costs have been found in Section 17 for 10^6 lb/hr flow. If one scales down using an arbitrary 0.7 power, a cost of $182/hr is found. If the feed concentration is 6,000 ppm phenol, about 1,600 lb phenol/hr are recovered. Assuming a sale price of 2.2¢/lb, this is $35/hr recovered. The energy is taken as 10^6 Btu/thousand gallons.

Ammonia separation is as used before. Since the feed has 12,000 mg/l ammonia, $218/hr are recovered from the sale of ammonia.

Distillation requirements are shown on Figure 15-7. For 0.8 × 10^6 gallons/day these are $132/hr and 1.5 × 10^6 Btu/hr.

Carbon adsorption costs, from Figure 15-1, are based on an assumed COD removal of 50 mg/l as discussed in Section 15.5

REFERENCES SECTION 19

1. Milios, P., "Water Reuse at a Coal Gasification Plant," Chemical Engineering Progress 71 (6), 99-104, June 1975.

2. Kleusner, J., Heist, J. and Van Note, R. H., "A Demonstration of Wastewater Treatment for Reuse in Cooling Towers at Fifteen Cycles of Concentration," presented at AIChE Water Reuse Conference, May 1975.

3. Skrylov, V. and Stenzel, R. A., "Reuse of Wastewaters--Possibilities and Problems," presented at the Workshop on Industrial Process Design for Pollution Control, AIChE, New Orleans, October 1974.

APPENDIX 1

ANALYSES OF WASTEWATER SAMPLES

Although analysis was not a major part of this study, we were fortunate to have received three sets of samples from the Institute of Gas Technology's Hygas pilot plant (two derived from Montana lignite and one derived from Illinois coal) and two sets of samples from Pittsburgh and Midway's Solvent Refined Coal pilot plant. Our analytical procedures follow*. The analytical results are given in Section 14. As is emphasized there, further analyses are essential for an economic design of a water treatment plant. When making our analyses we ran into some troubles and found some still unresolved inconsistencies which we have recorded here in hope of giving some assistance to future analytical programs.

Our samples were shipped to Cambridge, Massachusetts for analysis. One sample, shipped unpreserved from Fort Lewis, Washington, contained 0.5% phenol when shipped and only 0.0065% phenol when we analysed it. Even with waters as foul as these, preservation of a special sample for phenol analysis (using copper sulfate and phosphoric acid[1]) is necessary.

We had some trouble with total organic carbon (TOC) and chemical oxygen demand (COD) analyses. First we found that two different samples (both from Montana lignite), shipped unpreserved from the Hygas plant, gave

	Sample 1	Sample 2
COD (mg/l)	13,586	29,993
TOC (mg/l)	3,936	5,270
COD/TOC (calculated)	3.5	5.7
Sulfide	not analyzed	none detectrd

We have trouble justifying the high ratio COD/TOC in Sample 2. Either the TOC measurement is too low, which can occur if volatile carbonaceous molecules such as benzene are lost during sparging to remove inorganic carbon, or the COD is too high. If COD is too high, we are not sure what non-carbonaceous reducing compounds are present. An unpreserved sample from the Solvent Refined Coal plant gave

---

*Analyses were done by Dr. Judith Clausen.

TOC (mg/l)	6,600
COD (mg/l)	43,635
COD/TOC	6.6
Sulfur	10,500

but reduced forms of sulfur could account for the high COD.

When a sample is preserved for shipment by reducing the pH to less than 2 with sulfuric acid[2], then an extra sample must be separately preserved and shipped for sulfide analysis[2] and inorganic carbon and alkalinity cannot be determined. We received a preserved sample from the Solvent Refined Coal plant on which phenol, sulfur and nitrogen analyses had been performed, at the plant, before acidifying for shipment. We found

COD, mg/l as received	31,718
COD, mg/l sulfide removed	25,200
TOC, mg/l	7,390

Sulfide was removed by pH adjustment followed by addition of lead carbonate. Since the sample before preservation contained 16,200 mg/l sulfur, clearly some of the sulfide survived acid preservation. Sulfide removal reduced the COD/TOC ratio from 4.3 to 3.4.

Being disturbed by possibly high COD measurements, we tried to find whether the unusually large quantities of ammonia present could affect the COD analysis. We prepared a solution of 2.5510 grams potassium acid phthalate in 100 ml water (theoretical COD = 30,000 mg/l) and measured a COD of 29,676. To the same solution we added 5.00 grams ammonium carbonate and measured a COD of 29,472. However, we then took the ammoniacal solution, made it alkaline and bubbled nitrogen through to remove ammonia. After two hours bubbling the COD measured 33,263 and after three hours of bubbling the COD measured >38,060. We have no explanation for results obtained when we tried removing ammonia.

Finally, samples were shipped from the Hygas plant (from Illinois coal), one unpreserved and one split into three with part preserved with H_2SO_4 (for COD, TOC and nitrogen), part preserved for phenol and part preserved for sulfide. We found

	Preserved Samples (mg/l)	Unpreserved Samples (mg/l)
Nitrites - N	None detected	None detected
Nitrates - N	None detected	None detected
Ammonia - N	7,200	7,200
Sulfide	540.0	490.0
Sulfate	355.0	340.0
Phenol	273.4	265.4
TOC	702	3,573
Total Carbon	1,225	4,722
BOD - 5 days	--	2,682
BOD - 20 days	--	3,616
COD - as received	2,999	3,445
COD - ammonia removed	--	3,025
COD - ammonia & sulfide removed	--	2,686

Nonpreservation of the sample caused no loss of ammonia and some loss of sulfide and phenol. We cannot explain the effect of acid preservation on TOC and total carbon; the COD/TOC ratio in the preserved sample, being 4.3, is possible, but the ratio of 1 in the unpreserved sample seems quite impossible.

In closing, we point out that all of our BOD measurements were made on samples shipped unrefrigerated.

Analytical Procedures

General. Most of the procedures used were those from "Standard Methods" (Reference 1) which are usually the same as those of the EPA (Reference 2). Page references and specific detail, where helpful, are given in the following list. However, the basis of the method has not been copied from the reference; detail has been given only when a choice was made. The procedures used for water analyses at the trials of American coals in the Lurgi gasifier at Westfield Scotland (Reference 4) became available near the end of our work; we tried their method for chloride analysis and suggest that this reference be studied by someone embarking on analytical work.

A suggested list of procedures specific to coal conversion studies was published towards the end of our work (Reference 3). We find little difference between these recommendations and our procedures, and have tried to note those differences which we did find.

Biochemical Oxygen Demand. Standard Methods[1], page 489; EPA[2], #00310, page 11. Sample dilutions used were 0.5%, 0.2%, 0.1%, 0.02% and 0.01%. Dissolved oxygen was determined using the modified Winkler (azide) titration as described in Standard Methods[1], page 474.

Chemical Oxygen Demand. Standard Methods[1], page 495; EPA[2], #00340, page 20.

Total Carbon and Total Organic Carbon. Measured using a Dohrmann Analyzer Model DC-50. This machine measures total carbon directly and total organic carbon on a sample acidified with hydrochloric acid. Inorganic carbon is obtained by difference.

Alkalinity (total). Standard Methods[1], page 52; EPA[2], #00410, page 3.

Chloride. The method of titration with silver nitrate (Standard Methods[1], page 96) proved unworkable because the high concentration of organic matter caused the solution to darken with time. Sulfides also interfere. On a sample from the Hygas plant (using Illinois coal), we tested the following methods with the following results:

1) Reference 4, Method 6.12, page 296. Hydrogen peroxide is used to decompose the organic matter in the sample. Chloride is titrated with silver nitrate using potassium chromate as an indicator. 10 ml of water is diluted to 150 ml and boiled for 15 minutes with 10 ml of 30% (by volume) hydrogen peroxide. A second 10 ml of 30% H_2O_2 is then added, and boiling continued for another 5 minutes. The standard argentometric analysis did not give a satisfactory endpoint, so excess silver nitrate was added and the solution back titrated with thiocyanate using ferric ammonium sulfate as indicator.

2) As No. 1, except two 5 ml portions of 30% by volume hydrogen peroxide were used.

3) Argentometric method for chloride, Standard Methods[1], page 96. The sample was not pretreated. 5 ml aliquot was diluted to 100 ml. Sulfide and thiosulfate interfere with the titration. Hydrogen peroxide pretreatment removes the interference.

4) Dry-ashing Method for preparing food samples for analysis from Reference 5. 100 ml of sample is evaporated to dryness and then ashed in a muffle furnace at 525°C. The residue is taken up in dilute nitric acid and Method 3 used for titration. The dry ashing easily removes organic matter and sulfides. It may be necessary to evaporate samples larger than 100 ml to insure good accuracy as the method requires 20 mg of chloride for 1% accuracy.

Results:

	No. 1	No. 2	No. 3	No. 4
Chloride, ppm Cl.	236	360	263	233

Method 4 is particularly easy and seemed to give a satisfactory result.

Cyanide. Standard Methods[1], page 399; sulfide is precipitated with lead carbonate before distilling the sample. Cyanide is determined colorimetrically using pyridine pyrazolone reagent.

Ammonia. Standard Methods[1], page 224; sample distilled into boric acid and titrated with sulfuric acid.

Total Kjeldahl Nitrogen. Standard Methods[1], page 224; EPA[2], #00625, page 175.

Nitrite. Standard Methods[1], page 240; EPA[2], #00615, page 215.

Nitrate. Standard Methods[1], page 234.

Phenol. Standard Methods[1], page 502 (Distillation) and page 507 (Direct Photometric Method); EPA[2], #32730, page 241.

Sample distilled and the aqueous solution reacted with 4-aminoantipyrene.

Under ordinary conditions the Standard Methods procedures does provide for the removal of hydrogen sulfide by the addition of phosphoric acid (pH less than 4) and copper sulfate to the sample. We do not know whether all the sulfide is removed from the high sulfide containing samples using the quantity of copper sulfate recommended in Standard Methods. For precise and accurate analyses, this aspect of the phenol analysis should be investigated.

Sulfide. Standard Methods[1], page 551; EPA[2], #00746, page 284.

Sulfate. Gravimetric as $BaSO_4$, Standard Methods[1], page 331; EPA[2], #009471, page 283.

Metals. Calcium, magnesium, sodium, potassium, manganese, iron, aluminum, barium and silica were determined by atomic absorption spectroscopy. 100 ml of sample are taken to dryness on a hot plate. The residue is treated with 5 ml HCl and 5 ml HNO_3 and heated to dryness. This treatment is repeated three times. The residue is then quantitatively transferred to a 100 milliliter volumetric flask with deionized distilled water. Thus prepared, the samples were anlayzed using the methods described in the Jarrell-Ash Atomic Absorption Methods Manual[6]; these methods parallel those described in Reference 2. Potassium, sodium, calcium, magnesium, manganese and iron were determined using an air-acetylene flame whereas aluminum, barium and silica were determined using an air-nitrous oxide flame. To suppress ionization, suitable amounts (0.1-1%) of potassium or lanthanum were added to standards and samples of aluminum, barium and calcium; 0.1% cesium was added for potassium determinations.

Emission spectrographic surveys are based on 10 drops (0.5 ml) of solution. Each drop is individually dried with a sun lamp in the electrode crater.

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4. Woodall-Duckham, Ltd., "Trials of American Coals in a Lurgi Gasifier at Westfield, Scotland," pp. 276-302, NTIS Catalog FE-105, November 1974.

5. "Official Methods of Analysis of the Association of Official Analytical Chemists," Washington, DC, p. 296, 1975.

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